ELECTROLYTIC POLISHING
AND
BRIGHT PLATING OF METALS

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BY

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FOREWORD BY

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TO
MY MOTHER

FOREWORD

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ELECTROLYTIC polishing and bright plating—whether they be regarded from the economic or the scientific standpoint—may fairly be classed among the achievements of the present century. It was a happy thought to bring together a discussion of the two subjects within the covers of a single volume, since they contribute to the solution of the same technical problem. Either process can serve to reduce the amount of mechanical polishing needed in the production of plated articles—a matter of real economic importance at the present time in view of the high cost of surface treatment when carried out by mechanical methods.

Owing to the pressing need to develop the export trade of our country, special interest attaches to processes which enable a satisfactory and attractive surface finish to be obtained at minimal cost. It is by surface finish that a potential customer largely judges the quality of an article; however well designed and robust it may really be, any inferiority of finish is likely to cause rejection. But this is only one reason for developing methods of obtaining bright flat surfaces. There exist cases where smoothness may be essential, not merely to the attractiveness of the newly purchased article, but to its practical utility over long periods. Reflectors and bearing surfaces are examples which spring to mind, but there are others. It is no coincidence that, in recent years, several Congresses have assembled—at Paris and elsewhere—to discuss in detail the *États de Surface.*

Evidently, methods which can produce mirror-like surfaces, without a large amount of mechanical surface treatment, must present very real interest to manufacturers at the present time. It should, however, be pointed out that bright plating and electrolytic polishing are not just cheaper methods of achieving the end reached by the older process. They differ from the latter in kind. The material applied during a bright plating process usually possesses a different composition from that applied during an ordinary plating process, owing to incorporation of the brightening agent, and sometimes the co-deposition of a second metal (*e.g.*, cobalt in certain bright nickel coatings). Similarly, electrolytic polishing differs essentially from mechanical polishing in that it depends essentially on the complete destruction of prominences, whereas mechanical polishing usually causes the material of the prominences to flow down and fill in the intervening valleys.

Scientifically speaking, electrolytic polishing depends on factors which are the reverse of those applied in bright plating. If electrodeposition is conducted without special precaution, there is a tendency for deposition to occur on microscopic projections rather than in the intervening recesses, for two reasons; first, the current will normally be higher and secondly, replenishment of ions will be more rapid, at prominences than elsewhere. Any successful method of bright plating must counteract these two factors and ensure that conditions for deposition are less favourable at incipient prominences than at the intervening recesses. In anodic polishing on the other hand, these two factors mentioned will tend to make anodic dissolution more rapid at prominences than elsewhere, and will thus help to make the surface smoother. It is likely that in many systems of electrolytic polishing, the fact—emphasized in the classical work of W. J. Müller at Vienna—that passivity tends to set in preferentially at stagnant places (such as the recesses of a rough surface) plays a real part in ensuring that attack proceeds preferentially at the prominences. Other factors undoubtedly play their part, and it is generally believed that different methods of electrolytic polishing depend upon different basic principles.

Nevertheless, electrolytic polishing can only be achieved under carefully controlled conditions. Applied without control, anodic attack usually renders a surface not smoother but rougher. Sometimes the attack proceeds in a manner dictated by crystal orientation, so that anodic etching produces a number of crystal facets varying in inclination on different grains; under other conditions, trenches appear along the grain boundaries, whilst in two-phase alloys one constituent may be attacked whilst the other is left in relief. In all these cases, the result is a roughening rather than a smoothing. In certain cases, anodic attack may even be confined to a limited number of points. Aluminium sheet coated with an oxide film, may, when subjected to anodic attack in certain solutions, suffer perforation at particular spots without any attack at all on the intervening surface; for when once the film has been destroyed at a given point, anodic attack there continues in preference to the places where the film is intact. Clearly, if we are to use anodic action to make the surface smoother instead of rougher, the conditions must be scientifically controlled, and Jacquet, the inventor of electrolytic polishing, has shown how the conditions necessary for polishing are related to the current-voltage curves.

Many papers have appeared on the theoretical and technical aspects of electrolytic polishing and bright plating; some have been printed in British journals—others in American or in French publications. It is, however, a curious fact that few books are available on this extremely important subject. Thus a volume by a highly qualified author, which brings together the essential facts within a reasonable compass, is likely to fulfil a most useful purpose. Dr. Wernick is peculiarly well fitted to write on this subject. He is acquainted with electrochemical processes both at the works and in the laboratory, whilst his efforts as Secretary, and later as President, of the Electrodepositors' Technical Society have contributed—perhaps more than anything else—to the successful development of that admirable Institution, from which has flowed a stream of publications dealing with research and practice in electrodeposition and allied processes —including, during recent years, electropolishing. Dr. Wernick's book should fill a very real need, and there is little doubt but that it will be greatly welcomed.

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April 22nd, 1948.

AUTHOR'S PREFACE

AT no time has metal finishing assumed so much importance as it possesses to-day. With the advent of chromium plating, in particular, the possibility of applying a stainless, durable and highly attractive surface to metal goods became feasible. In consequence, a very high proportion of metal goods, ranging from motor-cars and household furniture to jewellery and knick-knacks of all types, are finished in this way, both for home consumption and the export market.

It has been fully established that where competition is encountered in the sale of metal articles or articles carrying metal components, the quality and attractiveness of the finish represent selling points the importance of which cannot be over-emphasised in any market. In the ultimate resort, it is, after all, the appearance of an article which first catches the eye of the prospective customer, whether at home or abroad.

Manufacturers are fully aware of these facts, and in consequence electroplating processes have never been so much in demand in our factories. The production demands have been exceeding the quantities which electroplaters can supply. Apart from shortage of material and labour, there is one bottle-neck in particular which is probably more troublesome than all others—namely, the shortage of metal polishing plant and personnel. Chromium plating processes are dependent to a peculiar degree on the preparation of metal surfaces by polishing, and unless some relief in breaking this bottle-neck is forthcoming, metal finishers will literally not be able to " deliver the goods."

In this difficult situation the electro-chemist is now taking a hand, and already, as a result of intensive laboratory research, electro-chemical methods have been developed to by-pass mechanical polishing operations by substituting electrolytic means.

The attack of the electro-chemists has been along two independent lines. The first has been the development of bright plating solutions—electrolytes which deposit a highly lustrous metallic coating which needs no subsequent polishing, instead of a dull or matt deposit, which must be " buffed " or " finished " mechanically to produce the desired polish. Bright nickel plating, for example, is now widely practised. The deposition of other metals in the bright state, such as zinc, cadmium, silver, platinum metals, etc., has also been developed to the point of industrial application.

The second development—electrolytic polishing of metals—bids fair to be even more important than the first, in that the scientist's ultimate aim here is to establish a new method of polishing metal surfaces which completely eliminates the laborious and costly mechanical method which has been in use in our factories from time immemorial. While this is his aim, progress is necessarily slow and as an interim stage the electrolytic method has in some instances reached the point where if it does not eliminate the mechanical method completely, it can nevertheless supplement the latter considerably and materially reduce the time, labour and material which enter into the mechanical polishing operation.

The new technique is yet young but nevertheless full of promise, and has aroused enormous interest among harassed works managers as well as scientists and metallurgists.

The present work represents a first effort to produce a factual account of these important new developments in industry. So far as the author is aware, no previous book on the subject has appeared. The publication of this first edition, which is partly based on a series of articles published in "Sheet Metal Industries," has been somewhat delayed owing to present difficulties in the printing and publishing industry. A considerable mass of patent literature has grown up, especially that emanating from American sources; and an extensive bibliography is appended to this work to enable the reader to pursue his studies further should he so desire. Considerable effort has gone into the preparation of the bibliography which contains brief abstracts of the most important work—the object being to save the reader as much labour as possible in searching the literature.

As with all processes in their early stages of development, the useful information which may be gleaned from voluminous dissertations is apt to be disappointingly small. In the present work an attempt has been made to enunciate clearly the principles of electrolytic polishing and bright plating of metals, and to give useful working details of processes where they can be recommended. Where there has been any doubt of the usefulness of a process this has either been indicated or the data omitted.

AUTHOR'S PREFACE

Undoubtedly, as time goes on, as a result of the intensive efforts of laboratory workers, further material progress will be made, and it is hoped to incorporate such work in a future edition of this book.

The author would like to acknowledge the assistance of Mr. R. Pinner, B.Sc., in the preparation of the bibliography and in proofing the manuscript.

Thanks are also due to the proprietors of " Sheet Metal Industries " for permission to reproduce parts of the text.

S.W.

CLIFFHOLM, WOODSIDE PARK,
LONDON.

December, 1947.

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APPENDIX :

CHAPTER I.

The Development of Electrolytic Polishing

ONE of the most striking anomalies in industrial plating practice is the fact that two processes are often closely allied which otherwise differ very widely in every respect. These processes are the deposition process itself, based on electrochemical principles, and the polishing process, based purely on mechanical principles.

Unfortunately, up to now, it has not been possible to separate these processes, despite the fact that there can be very little doubt that the mechanical polishing of metals is a process which it would in every way be desirable to eliminate from the metal finishing sequence of operations. To enumerate a few of the disadvantages of polishing, one has only to point to the following facts.

DISADVANTAGES OF MECHANICAL POLISHING

Firstly, as a process, it does not add to the cleanliness of the metal finishing department, the maintenance of which, it is increasingly realised, is of the utmost importance in the production of good quality electrodeposits. Although quite efficient methods of exhausting the polishing dust, linters, polishing compositions, etc., have been devised and are commonly installed, nevertheless it seems to be impossible to prevent a fraction of these undesirable contaminants of the atmosphere from being wafted into the plating shop (which, usually, conveniently but not desirably, adjoins the polishing shop) and so find their way eventually into the plating solutions themselves with consequences which may vary from the very minor to the disastrous, according to the nature of the electrolyte involved.

Secondly, the polishing operation necessarily removes metal from the surface of the component being treated, and, while this may matter little in regard to the basis metal, it is of very vital consequence if the metal happens to be that which has just been applied in the plating vat. The absurdity of depositing a " thou." or more of nickel on steel in accordance with the latest concepts of providing a maximum of corrosion resistance and then removing perhaps half or more in the polishing operation prior to chrome is so evident that it requires no further embellishment. In this connection, of course, the advent of bright nickel plating has very largely proved to be the answer to this particular problem. However, there is nevertheless a considerable amount of dull nickel plating still being carried out in the majority of shops in this country; while again, the bright nickel process cannot be considered as universally applicable to all types of components, and even where it is definitely applicable, a certain amount of " light mopping " still requires to be carried out before chromium plating.

Lastly, possibly the biggest disadvantage of all, is the cost factor. There is very little doubt that mechanical polishing is one of the most costly operations in the metal finishing cycle; for example, typical costs show that the total cost of polishing the basis metal, nickel finishing and final chrome finishing, can work out to as much as three to four times the total cost involved in the preparatory cleaning and plating operations.

It will therefore be agreed that this represents a severe indictment where this process is allied to plating operations. Unfortunately, it has not been possible to do very much to obviate or reduce the amount of polishing involved in the bulk of metal finishing—other than that which has been accomplished as a result of bright plating processes. Any process, therefore, which can result in reducing the amount of mechanical polishing, is obviously one in which all platers must be intensely interested. This possibility is now being vigorously explored, since a process which may result in eliminating such mechanical polishing has, in fact, been evolved and is now in course of development with a view to increasing its sphere of application in industrial practice. It is a singular fact that this process is itself an electrolytic one, and, as such, the essentials of the process have, in fact, been available to electroplaters in their own plants during the whole of the time that they have been forced to employ those mechanical methods which carry so many radical disadvantages in their operation.

ORIGINS OF ELECTROLYTIC POLISHING

It is even possible that platers in the past have on occasion observed the phenomenon of electrolytic polishing without attaching too much importance to the occurrence. The process where such observations may have been made, in particular, is that of stripping base metals of faulty nickel deposits by anodic etching in a sulphuric acid electrolyte. The author can certainly testify to the fact that he has been frequently struck by the fact that as the removal of the nickel proceeded so did its brilliance or lustre often increase. The phenomenon can be particularly noted on smallish articles, or, alternatively, those parts of the component which protrude or are angular and, being nearest to the cathode, receive a higher current density than other parts of the surface. In particular, where nickel coated hooks are employed, carrying work to be stripped in the denickelling operation, such hooks may be observed to attain a high degree of lustre, due to the fact that, the area of these hooks being very small, the current density is correspondingly high and the conditions are such as to produce electrolytic polishing of the surface. On the other hand, on such parts of the surface where the current density is low no such polishing action occurs. It will thus be seen that one of the essentials in the production of a polished surface by electrolytic methods, is that the current density shall exceed a certain given minimum, this latter depending on the special conditions pertaining in a given case.

A somewhat interesting question which arises in connection with the above observations is this: Who first observed the phenomenon of electrolytic polishing? Was it the chemist in the laboratory or, as the author considers much more probable, some humble plater in the shop, who, having observed the phenomenon, did not think it worth while to record the event?

As regards observations of the laboratory, many references may be found in the literature over a period of the last 20 years or so, although some of them are merely oblique references indicating that a change in the surface appearance had occurred; *e.g.*, a brightening effect may have been observed, but it may not specifically have been stated that polishing had taken place.

THEORETICAL BASIS OF ELECTROLYTIC POLISHING

In all electrolytic polishing operations the article which is to be so treated is made to act as the anode in a suitable electrolytic circuit. Metals react differently to such anodic treatment depending on their nature; for example, there are exceptional cases where the metal is entirely unattacked, as in the case of platinum; here, oxygen only is evolved, but the platinum undergoes no chemical change.

The change here may be represented by the following equation :—

$$H_2O = 2H^{\cdot} + O''$$
$$\text{Pt.} \longrightarrow \text{Pt.}$$

Again, the metal may react with the anions, in which case one of two things will occur.

(1) The product of reaction is soluble, as in the case of copper in an acid copper sulphate electrolyte, when continuous solution of the anode will then occur. The corresponding equation may be written as follows :—

$$Cu + H_2SO_4 = \underset{\text{(soluble)}}{CuSO_4} + 2H^{\cdot}$$

(2) On the other hand, if the product of reaction is insoluble *e.g.*, if silver is made the anode in a sodium chloride solution, the insoluble silver chloride formed soon prevents any further passage of current and the reaction stops in a short time. The following represents the reaction :—

$$Ag + NaCl = \underset{\text{(insoluble)}}{AgCl} + Na^{\cdot}$$

Still a further possibility is for a soluble salt to form which concentrates in the vicinity of the anode surface, forming a thin viscous film which, if undisturbed, may interfere with, but not stop, the continuous solution of the anode as a whole. Now if this viscous film varies in depth over the surface, as would be the case where pockets are formed through the contour of the surface not being an absolutely straight or unbroken line, then less interruption of the current will take place at those points where the film is thinnest—*i.e.*, where the contour protrudes towards the cathode. If, therefore, it is considered that a polished surface has a straight line contour, whereas a matt surface consists of a series of local crests, it will be apparent that the action which occurs in the electrolytic system described above is that of gradually eliminating these crests. This, accordingly, is the underlying principle of electrolytic polishing of metals.

If now one compares what takes place in mechanical polishing with the action in electrolytic polishing, the difference is very profound. In mechanical polishing there is produced a flowed amorphous surface (known as the Beilby Layer). In electrolytic polishing, on the other hand, the "high lights" are gradually removed, the surface being progressively smoothed, a close analogy being the action of the sea on rough pebbles, or, better still, the smoothing of the surface of a sweet when continuously sucked in the mouth.

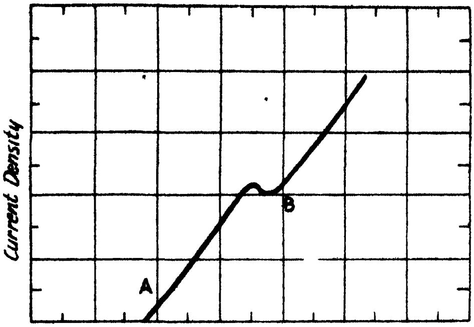

Fig. 1.—Typical current density voltage curve in electrolytic polishing.
A. Decomposition voltage B. Critical voltage

HISTORY OF THE PROCESS

However long ago the first observation was made of the electrolytic polishing action, no reference appears to have been chronicled before the year 1925 or thereabouts, and then it took the form of a somewhat oblique reference by C. P. Madsen (1) who, at that time, was working on the production of high-quality electrodeposited nickel on steel. To obtain satisfactory adhesion, he used the bath containing concentrated sulphuric acid at a current density of about 100 amps./sq. ft. Madsen noted that this resulted in the production of a white pearly surface on the steel. Some three years later, two investigators, R. M. Burns and C. W. Warner,(2) took out a patent for an anodic electro-cleaning process. They used 70 to 100 per cent. phosphoric acid as an electrolyte and a current density of 100 amps./sq.ft. for three minutes, and recorded the fact that under certain conditions bright surfaces were obtained on the steel. N. R. Laban,(3) in 1930, before a meeting of the Electrodepositors' Technical Society, specified an anodic treatment in a 30 per cent. sulphuric acid bath to which is added a small quantity of potassium dichromate, again as an etching operation to help adhesion of nickel to steel. He noted the production of a clean satin finish resulting from this treatment. G. B. Hogaboom,(4) in 1932, took out a patent for a process which he termed "Electrolytic Bright Dipping" on iron and steel. In this process the steel, after it has been descaled cathodically, is made anodic in the sulphuric acid bath, the concentration of which may vary from 25 to 75 per cent., operated at current densities from 80 to 250 amps./sq. ft. According to Hogaboom, brightening action on the steel surface arose through the local formation of persulphuric acid. A couple of years later, C. G. Fink and F. J. Kenny(5) took out a patent for the treatment of metals to increase their resistance to corrosion. They used chromic acid solution, specifying that an oxidising electrolyte was necessary. While they did not lay stress on the appearance of the surface, the articles so processed were claimed to have very high corrosion resistance, arising through the passivation of the surface resulting from the treatment.

Next comes the very important work of Jacquet,(6,7) who made a very careful study of the phenomenon of electrolytic polishing from 1935 onwards. In his first experiments, Jacquet used copper as the basis metal and obtained a mirror finish, using orthophosphoric acid as the electrolyte. Later, he extended this work to several other common metals, and in particular to brass, lead and tin. For these metals Jacquet developed an electrolyte which he used extensively, namely, a mixture of acetic and perchloric acids in various proportions to suit the metal to be polished

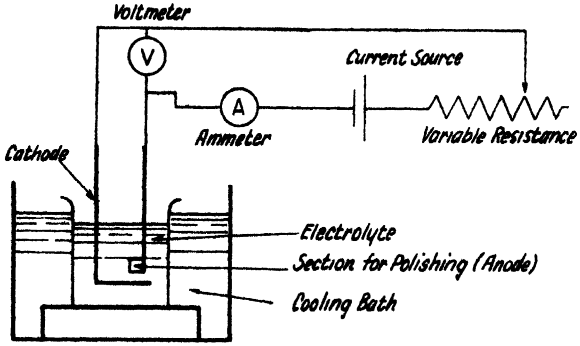

Fig. 2.—Typical circuit for electrolytic polishing

It should be made clear that Jacquet was not concerned with the production of polished surfaces for industrial uses, but practically exclusively with using an alternative to mechanical polishing in obtaining a polish on small samples of metals purely for metallographic purposes. It should be appreciated that the problems involved in producing an adequate degree of polish on a very small area of metal, usually less than a square inch in area, become very much more complicated when such a polish is to be applied to metal components not only very much greater in area but also varying considerably in shape, contour, etc. Nevertheless, the work of Jacquet was highly important, as it pointed quite unmistakably the road leading to the production of polished surfaces for industrial purposes. It should be added that it was Jacquet's theory that the anodic corrosion product forming on the surface (*i.e.*, the metallic

TABLE I

ELECTROLYTES EMPLOYED BY JACQUET FOR ELECTRO-POLISHING

Metal.	Electrolyte.	Current Density. (amps./ sq.dcm.)	Voltage
Copper .. .	Pyrophosphoric Acid 530 grm. per litre.	8 to 10	1·6 to 2·0
Brass (70–30) (1 constituent)	Orthophosphoric Acid 430 grm. per litre.	13 to 15	1·9
Brass (60–40) ... (2 constituents)	Pyrophosphoric Acid 530 grm. per litre.	9 to 11	1·9
Lead	Acetic Acid 650 to 750 c.c. Perchloric Acid 350 to 250 c.c.	1 to 2	Not stated
Tin	Perchloric Acid (S.G. 1.61) 194 c.c. Acetic Anhydride 806 c.c.	9 to 15	25 to 40
Aluminium	Perchloric Acid (S.G. 1.48) one part Acetic Anhydride 2 parts to 7 parts.	3·0 to 5·0	50 to 100
Steels (1) ... ... Carbon Steels.	Perchloric Acid 185 c.c. Acetic Anhydride 765 cc..	4 to 6	50
Austenitic Steels ...	Perchloric Acid (65 per cent.) 1 part. Acetic Anhydride 2 parts.	0·6	0·75 to 2·0

salts forming as a result of action with the electrolyte) which accumulates in the depressions of the contour caused corresponding local passivity, and that this results in the "projections," which are more active, being preferentially dissolved until a smooth surface is produced.

Table I, shown above, is a summary of the conditions which Jacquet determined for the production of electro-polished sections of the various metals indicated. The object in each case was to produce a polish on a section purely for subsequent micrographic examination. It is not proposed, however, to deal any further with this specialised application of electrolytic polishing, but to turn to the type of application which is interesting to the metal finisher.

Before, however, proceeding to do so, it will no doubt be interesting to point out one or two of the advantages which electropolishing possesses over mechanical polishing. For one thing, the local heat which is generated on a metal surface which is mechanically polished is obviated. This prevents distortion of the surface and is incidentally a very valuable feature in the preparation of metallographic specimens, as the crystal structure is revealed in an unstressed or distorted condition when the surface is subsequently etched. Furthermore, all constituents of the material examined are on the same macrographic level, whereas mechanical polishing may adversely affect the softer constituents which may be present. Another important advantage is the fact that the process is speedy and to a large extent independent of the size of the article being polished. As is well known, in mechanical polishing, the time required to produce the requisite polish increases rapidly with the size of the article to be polished.

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CHAPTER II.

Electrolytic Polishing of Stainless Steels

THE present position as regards the industrial applications of electrolytic polishing is that while undoubtedly the process is basically to a great extent still in its infancy, it has already been applied fairly extensively in certain fields which facilitate the process for one reason or another. In the author's opinion, however, there is no real reason why, in the long run, practically every common metal may not lend itself to electrolytic polishing; in particular, copper, nickel, aluminium, zinc, tin, lead, and brass represent base metals which are more or less promising in their ultimate industrial development. It is true that in some cases the electrolytic polishing operation may require some degree of assistance by the use of mechanical polishing, either before or after the electrolytic treatment, depending on such factors as the composition of the material; the impurities therein; the initial state of the surface, etc., but in the long run, it is likely that every one of these metals will reap some degree of benefit from electrolytic polishing.

In actuality, most attention has been focussed to date on the possibilities of electro-polishing stainless steel, although it may be said that only slightly less interest has been aroused by the possibilities that exist with aluminium as a basis metal.

A considerable amount of work has already been carried out in investigating the possibilities of electro-polishing stainless steel, as there is an obviously big field here due to the increasing popularity of this material in the manufacture of many types of components during the last decade or two. While stainless steel provides a varying degree of corrosion resistance depending on its constituents, the possibilities that exist for its decoration are strictly limited. Most usually, the decoration takes the form of applying as high a polish to the surface as can be obtained by using the available polishing compositions, etc. Unfortunately, most stainless steels are relatively tough, and because of this, do not lend themselves to easy polishing by mechanical means. The polishing operation, as a result, is invariably relatively expensive both in material and labour, and hence, any alternative method of obtaining a similar finish which is more economical, holds obvious attractions.

The electrolytic polishing of stainless steel has reached the industrial stage mainly in the United States, and while several electrolytic processes have been proposed, there are two in particular which have enjoyed a considerable degree of success, and have the advantage of being based on relatively simple electrolytes. The two main electrolytes consist essentially of phosphoric and sulphuric acids respectively, to which are added "addition agents" which considerably facilitate the electrolytic action. In the case of phosphoric acid, glycerine is one of the most successful addition agents, while sulphuric acid is coupled with an organic acid, for example, citric acid. Other solutions which have been suggested, contain mixtures of phosphoric and sulphuric acids. It is proposed, however, to deal with the two basic types of solutions in this Chapter.

PHOSPHORIC ACID PROCESS

H. H. Uhlig* developed a process based on phosphoric acid in 1940, and found that the optimum concentration of the constituents of the electrolytes consisted of a 90 per cent. solution, with rather more glycerine than phosphoric acid, the balance being water.

Uhlig comprehensively determined the effect of the various factors, such as temperature, current density, etc., and his findings may be summarised as follows :

The effect of temperature was found to be quite appreciably important, a higher range of temperature giving markedly better results. In this range, metallic loss was reduced and pitting eliminated to a great extent. In point of fact, the most highly-polished surfaces were obtained when the solution was used somewhere in the region of boiling point.

As regards current densities, it was found that the best results were obtained when these were relatively high. In the lower range of current densities, *e.g.*, below approximately 20 amps. per sq. ft., it was found that there was more anodic solution of metal from the surface, probably due to local etching. Current densities as high as 100 to 200 amps. per sq. ft. are actually found to give best results consistently producing highly polished surfaces.

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* H. H. Uhlig, *Trans.* Electrochem. Soc., 1940, 78 (Preprint).

The relationship between voltage and current density in an electrolytic system producing the polishing action is very typical, and was shown in Chapter 1. As the voltage rises, so there is a corresponding increase in current density, until it eventually reaches a critical value, when there is a sudden drop in the current density with a corresponding voltage increase. Thereafter, there is again a steady rise in current density with increase in voltage. Normally, it is at this critical point that the anodic change takes place, and it is often marked visually by a surface change in colour. The anodic polishing action takes place when the current density is held at points beyond this critical turn in the curve. The effect of current density and temperature on the specular reflectivity is shown in Figs. 3 and 4, respectively.

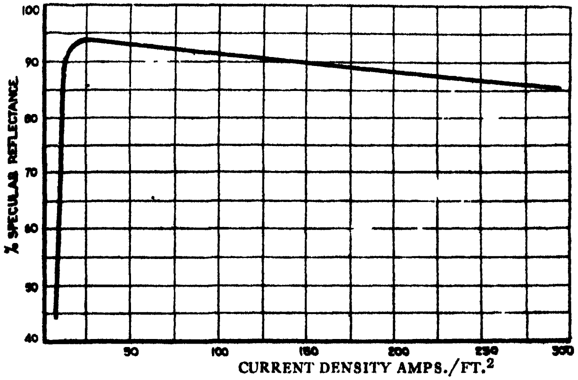


Fig. 3.—Effect of current density on specular reflectance. Material 18/8 stainless steel, solution phosphoric acid/glycerine (after Uhlig)

The use of the high-current densities, mentioned above, *i.e.*, in excess of 100 amps. per sq. ft., obviously presents some practical problems which, while they are not beyond solution, are troublesome, and must be dealt with suitably in order that the process may be placed on a practical footing. In the first place, it is necessary to make use of a motor generator, or, alternatively, a rectifier which is capable of providing up to about 15/20 volts in order to supply the necessary current. However, the use of high-current densities is no longer a novel feature in ordinary industrial plating practice, as similar current requirements have been met with in the production of chromium-plating. Indeed, the requirements are parallel to some extent in other respects, for example, it is necessary to ensure that correct jigging or wiring is employed, the section of the latter being adequate to allow for the requisite current-carrying capacity of the component which is being processed. As with chrome, good positive contact with the article is essential, since otherwise electrolytic action may take place at the point of contact.

It has been claimed that it is possible to employ an electrolyte in which the wire or jig material remains practically unattacked, due to polarisation, but it is preferable to employ stop-off materials for the jigs, as in plating practice, the nature of the material employed depending on the electrolyte which it has to resist; for example, insulating tape sprayed with a good quality high-viscosity lacquer would be found to be adequate for many purposes. Incidentally, stop-off lacquers have also been employed on the surface of the article itself in order to produce special designs in which the matt and polished surfaces contrast very effectively. This opens up a prospect of a pleasing and novel type of decoration which, so far as the author is aware, has not previously been employed with stainless steels, and will be referred to later.

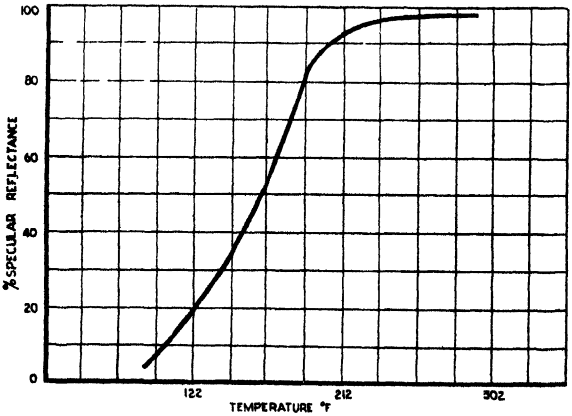
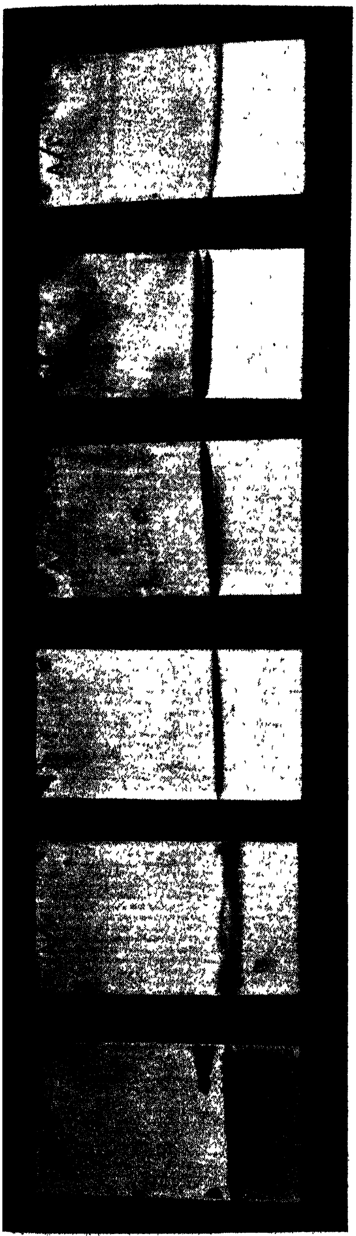


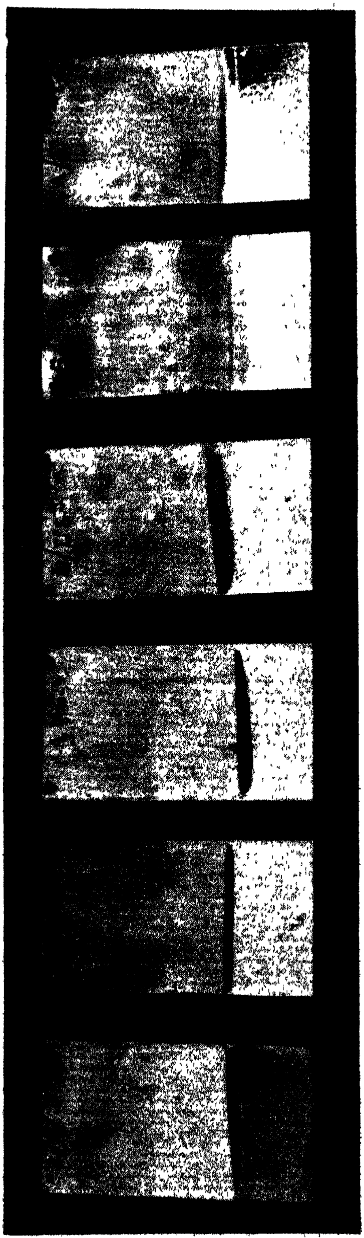
Fig. 4.—Effect of temperature on specular reflectance. Conditions as Fig. 1 (after Uhlig)

DEGREE OF POLISH AS AFFECTED BY THE BASIS METAL

It is important to note that a very wide range of stainless steels is available for manufacturing purposes in industry, and the electro-



Electrolytic polish. Phosphoric acid glycerine solution Fig. 5. Stainless steels (various)



Electrolytic polish. Citric acid/sulphuric acid solution Fig. 6. Stainless steels (various) as in Fig. 5

polishing action of a given electrolyte varies almost as widely in its efficacy as the actual range of material available.

Experiments carried out by the author in this connection have shown that one of the best materials to employ is a straight 18-8 stainless steel (containing practically no constituents other than iron, chromium and nickel), as increasing addition of other metallic constituents—*e.g.*, copper, tungsten, manganese, molybdenum, titanium, etc.—reduces the degree of polish obtainable.

In Table II is given some indication of the effect of alloying constituents on the degree of polish obtained. This does not necessarily rule out the possibility of producing an electrolyte which is, so to speak, tailor-made to the particular sample of stainless steel under consideration, and which will thus produce a far better polishing action than that obtained in the Uhlig bath, which was that employed in the author's experiments.

TABLE II

EFFECT OF ALLOYING CONSTITUENTS ON 18-8 STAINLESS STEEL

No.	Additional Constituent	Degree of Polish.*
1	None	Good polish.
2	Upwards of 0.5 per cent. copper...	Good polish, but inferior to No. 1.
3	Copper, 0·5 per cent. ... ... Tungsten, 0·5 to 1·0 per cent. Titanium—less than 1 per cent. ...	Fair polish; some etching.
4	Copper, 0·5 per cent. ... ... Tungsten, 1·0 per cent.	Mild polishing action.
5	Molybdenum, 3 to 4 per cent. ...	As No. 4, but additional bloom.

*The variation in the degree of polish obtainable is shown in Figs. 5 and 6 respectively.

It is an interesting fact, however, that the comparative degree of polish obtained with varying stainless steel alloys was very similar when an electrolyte based on sulphuric-acid and citric acid was employed in place of the phosphoric acid and glycerine solution (see Figs. 5 and 6).

SULPHURIC ACID ELECTROLYTE

Sulphuric acid type electrolytes have certain advantages over phosphoric acid as a basic ingredient of electrolytic polishing solutions, but there are also corresponding disadvantages, and the respective merits of these are discussed below.

In one well-known process the electrolyte consists of some 20 per cent. sulphuric acid with about 50 per cent. of citric acid, the balance being water. The solution is operated at a temperature exceeding 170° F., and up to about 200° F. As regards current density, this may be as low as 80 amps. per sq. ft., but better results are obtained at the higher ranges, which may even exceed 200 amps. per sq. ft. The time of treatment varies depending on the component to be processed, its shape, size, composition, etc., but normally it is brief and does not exceed 5 to 10 minutes.

A welcome characteristic of the sulphuric acid type electrolyte is that the current requirements are found to be less exacting. Thus considerably lower voltages may be employed to achieve the necessary high current densities as compared with those based on phosphoric acid.

Nevertheless, while sulphuric acid electrolytes possess some useful characteristics, it was found that the phosphoric acid based electrolyte consistently produced a superior degree of polish in practically every case. It is interesting to examine the action at the anode in each case.

The phosphoric acid-glycerine system is said to be particularly advantageous compared with the sulphuric acid system in that the anodic products of the electrolytic reaction—*i.e.,* metallic phosphates—are soluble in the electrolyte which is employed. As a result, a viscous layer is formed over the anode surface diffusing only slowly into the main body of the electrolyte.

On the other hand, sulphates which are the products of reaction in sulphuric acid electrolytes are considerably *less soluble* than phosphates—*i.e.,* in the more concentrated sulphuric acid solutions. For example, ferrous sulphate is not at all readily soluble (although it may be noted that it is fairly soluble in *dilute* acid). Hence, as a result, the viscous layer in contact with the anode is not so readily formed owing to its limited solubility, and this in turn may quite conceivably affect the mechanism, and, eventually, the efficiency of the process.

Fig 7

As for the glycerine which is present in the electrolyte, it is probable that it forms a complex with the phosphoric acid which is less conducting than phosphoric acid alone. The solution certainly possesses less conductance than the acid alone, and it is, therefore, possible that metal compounds formed from this complex may form an anodic film contiguous to the anode which is more efficient in its polishing (or smoothing) action than the acid alone. The action of the glycerine is not dissimilar to that of an addition agent which is frequently added in plating practice, in order to reduce grain size or to obtain a higher degree of lustre on electrodeposits produced at the cathode. In electrolytic polishing, this action takes place at the anode.

However, since no direct comparison of the two types of solution has, so far as the author is aware, been made on an industrial scale on the same type of component, it is not possible to state positively that one is superior to the other. Nevertheless, the above remarks are pointers to the relative advantages and disadvantages which each electrolyte possesses.

A further important and useful effect of the glycerine (or other organic addition agents which may be employed) is its inhibiting effect in preventing chemical attack by the electrolyte on the anode surface; this is particularly important in view of the high temperatures which are normally employed.

However, this is not the whole of the story; for, while the formation of more or less insoluble reaction products is not a good feature of sulphate type electrolytes, it has on the other hand been pointed out that the precipitated sulphates which form at the anode fall to the bottom of the tank and these can be removed periodically. It has been suggested that in this way the relative insolubility of the reaction product is thus a valuable factor in increasing the life of this type of bath, in that it is readily removable. It is a fact that in phosphoric acid type electrolytes the soluble phosphates do eventually increase the resistance of the solution. As a result, increasing voltages are necessary to maintain the requisite current densities.

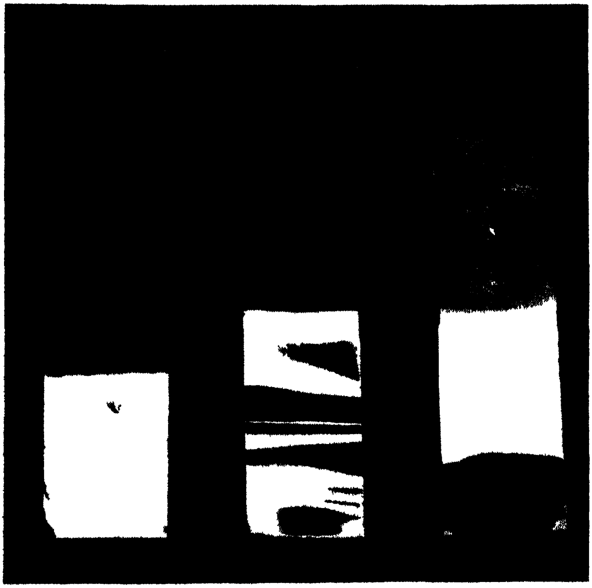


Fig. 8

Illustrating the respective throwing power of the phosphoric acid/glycerine bath as against the citric acid/sulphuric acid bath. This is shown by the matt area in the angle of the middle specimen in each set. Note superiority of specimen in Fig. 8 over that in Fig. 7

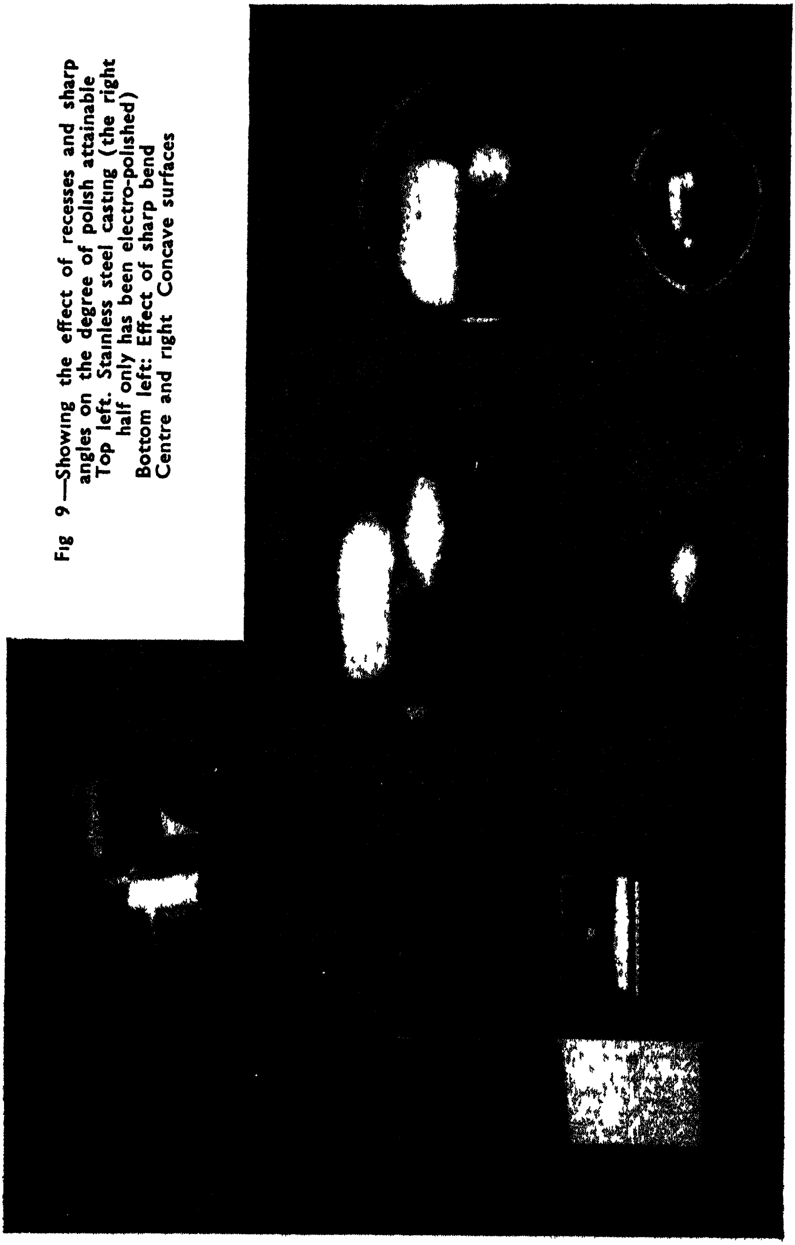


Fig 9.—Showing the effect of recesses and sharp angles on the degree of polish attainable
Top left. Stainless steel casting (the right half only has been electro-polished)
Bottom left: Effect of sharp bend
Centre and right Concave surfaces

However, this can be countered by the addition of further quantities of phosphoric acid periodically; the increasing voltage is thus arrested, but it never falls to that which it was possible to employ initially, hence, there is progressive deterioration and in time, the solution has to be discarded and a fresh one prepared. Probably, therefore, the sulphuric acid electrolyte has a longer life than the phosphoric acid bath. It has, in fact, been claimed that the former type of solution has been in use for as long as two years without necessitating complete renewal, being replenished from time to time to allow for drag-out losses and sulphate precipitation.

AUXILIARY MECHANICAL POLISHING

An important question which arises is the following: At what point and to what extent is mechanical polishing a useful asset as an aid to electrolytic polishing?

To obtain the best possible results, undoubtedly, some initial mechanical polishing treatment is usually desirable. As to the degree of mechanical polishing which should be carried out, this will vary with the type of component and is largely a function of the economics of the total polishing sequence. For instance, it may be more economic to produce a fairly highly finished surface in the first place, because this will not require any subsequent polishing treatment after anodic polishing; in another case, on the other hand, it may be more advantageous to reduce the initial mechanical polishing treatment to a minimum, and finish off the anodically treated surface by a light buffing operation, bringing the lustre up to the requisite pitch. The more expensive polishing operations are undoubtedly those which are initially applied to the metal surface, and so the fact that a light final polishing operation may be necessary may still make the whole sequence economically desirable and eminently worthwhile in a given case.

INFLUENCE OF SHAPE

Another important factor is the shape of the article. In general, a curved or contoured surface is more adaptable to electro-polishing methods than a plain flat surface. This is due to two factors —first, the difficulty of maintaining a uniform current density over a large plain flat surface, and, secondly, the fact that a concave or convex surface does not show imperfections so readily as those on flat surfaces.

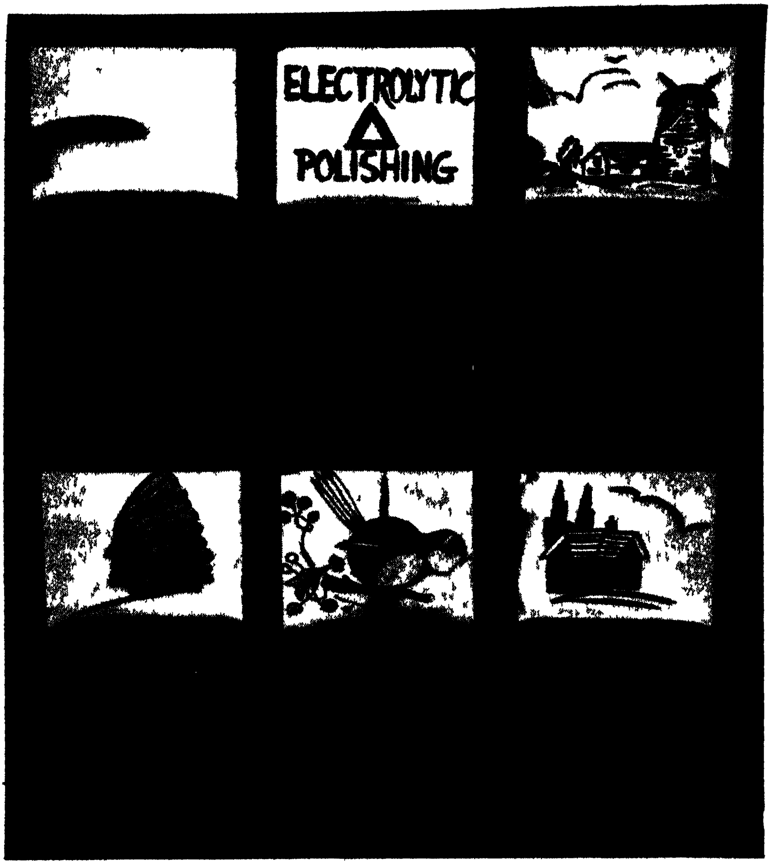


Fig 10—Decorative effects obtained on stainless steel by ' stopping-off "
prior to electrolytic polishing

On the other hand, sharp angles, recesses, bends, etc., are not desirable, as the throwing power of the solution, while reasonably good, is not sufficient to maintain the polishing effect at a sharp angle (see Figs. 7 and 8). This is not an unexpected feature, as it will be appreciated that the current density falls off very rapidly as the angle is approached, and it may easily fall below the critical value at which polishing commences.

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ELECTROLYTIC POLISHING OF STAINLESS STEELS

While the electrolytic polishing action has also been found to confer an appreciable degree of protection to the basis metal, very interesting possibilities exist in decorative effects, which can be produced by stopping-off portions of the surface so that the contrasting effect of matt and polished steel is emphasised in an attractive manner. It is possible, in this way, to produce attractive designs of all kinds. Some of these produced in the author's laboratory are shown in Fig. 10. Not only is it possible to obtain sharply contrasting effects, but these may be moderated by toning or softening by means of corresponding variations in the stopping-off technique.

SOME PRACTICAL DIFFICULTIES

It will be clear from what has been already stated that there are certainly a number of practical difficulties in the present state of development of the electro-polishing of stainless steel. These may be summed up as follows:—

First, there is the importance of maintaining the optimum conditions of operation in a given instance, which have been ascertained for a particular type of stainless steel. These must be maintained with reasonable closeness on a production scale. The composition of the electrolyte will alter with use, through evaporation losses, drag-out losses, contamination due to impurities which are brought into the solution, etc. These factors may result in the solution being thrown out of balance, and it may, in fact, be necessary to replace the initial optimum operating conditions by a new set of conditions at a later stage, or, alternatively, to start with a fresh solution. This, therefore, introduces a factor of uncertainty which may be negligible and unimportant in some cases, but may fundamentally affect the degree of polish attainable in others, largely depending on the nature of the component.

Secondly, the shape and contour of the article to be polished will affect the ultimate degree of polish attainable. Again, it may be possible to produce a tailor-made solution for a particular type of component.

Thirdly, high-current densities are required which necessitate rather heavy power supply arrangements for production loads.

Fourthly, difficulties may be entailed in maintaining the somewhat high temperatures which are usually necessary in the electrolytic bath. If these appreciably exceed 80° to 90°C., there are practical difficulties due to high evaporation losses, etc. There is also need for exhaust arrangements for steam given off from the solution. This being so, all methods of conserving heat are well worth employing in order to maintain the temperature—*e.g.*, lagging of tanks, covering up the solutions overnight, etc.

In spite of all these difficulties, it may be said that the anodic polishing of stainless steel has reached the point where it can be considered to be an established process. Although it has so far only been employed on a limited scale, the scope for widening the field of application is obviously very considerable, and it should interest all those who make use of such material for manufacturing a considerable number of components.

CHAPTER III.

Bright Nickel Plating

VARIOUS types of electrolyte have from time to time been proposed for the commercial production of bright nicked deposits. While, however, it is readily possible to achieve a relatively thin nickel deposit which is bright, the production of good quality bright nickel of a thickness interesting to commercial works production conditions is by no means a simple matter, and in point of fact, so far as this country is concerned, only two types of solution within the orbit of practical plating have proved to be successful under operating conditions. These are based fundamentally on the addition of cobalt and aromatic sulphonic acids respectively, and will be referred to in detail later.

The difficulties of producing a suitable electrolyte may be appreciated from the fact that it must, as has been well pointed out(1) as nearly as possible possess the following characteristics :—

(*a*) It must be capable of producing a highly lustrous or brilliant deposit within a fair range of current densities and to any commercially specified thickness.

(*b*) The exercise of simple analytical control must be possible so that this may be safely left to a junior works chemist if necessary.

(*c*) It must operate at high current densities so that speedy deposits may be produced—an essential requisite of modern mass production conditions.

(*d*) As wide a range of operation as possible is preferable, so that it may readily cope with changes in *p*H, current density, temperature, etc., which must not be too critical.

(*e*) The production of as uniform a deposit as possible on articles of relatively complex shape, such as are met with in common practice, is necessary—*i.e.,* the electrolyte must possess reasonably good throwing power.

(*f*) It should be exceptionally stable and not easily upset as a result of minor deviations from the specified operating conditions.

(*g*) It must be readily controllable by replenishment of the bath with regular and periodic additions of the constituents as they are used.

(*h*) Finally, the electrolyte and process must be readily adaptable to fit into existing plant layout of a modern type, so that where facilities are readily available for filtering, heating and agitating the plant, these may be readily serviceable with the minimum of strain on the plant engineer.

In addition to the above catalogue of requisites which a bright plating process should possess, the properties of the resultant deposit are not uncritical. It is essential, of course, that this deposit shall be mirror-bright (the production of a semi-bright or lustrous deposit which is all that is attained in a number of so-called bright nickel processes is not sufficient) while, furthermore, this mirror brightness must be attainable irrespective of the thickness of the deposit—although normally modern specifications would call for something of the order of 0·001 in.

Secondly, the deposit must possess good physical properties. Thus, it must be highly adherent, reasonably hard, fairly ductile, and free from porosity and other surface imperfections. Other desirable properties will arise by satisfying the requisites of the process outlined above—*e.g.*, good throwing power will ensure that the corrosion resistance imparted by the deposit to the basis metal is adequate, etc.

ADVANTAGES OF BRIGHT NICKEL

The general advantages accruing from bright nickel plating are fairly well known now. In the main, there are two important advantages, arising from (*a*) the mirror brightness conferred on the deposit; and (*b*) the high rate of deposition which is usually possible.

With regard to (*a*), sufficient has already been said in Chapter I on the importance of eliminating the polishing operations. Obviously in addition to the saving of labour and time an added saving which may often be achieved is the unjigging and rejigging which normally takes place between the dull nickel plating and chromium plating processes. There is, furthermore, the saving in thickness of the deposit which is normally removed in buffing nickel, and the risk of cutting through sharp edges either in the nickel buffing or final buffing operation, is eliminated.

BRIGHT NICKEL PLATING

The possibilities of speeding up the nickel plating process have been fully realised in practice; thus, where previously current densities of the order of 20 to 25 amps. per sq. ft. were normal, these have been increased to double these figures (and even more in special cases) and the plating time correspondingly reduced. There is no doubt, therefore, that bright nickel plating as an operation is worth while from every point of view and applicable to the majority of plated products. So much is this the case, that the author is of the opinion that except for such special applications of nickel deposition as necessitate the production of a deposit of specified characteristics—*e.g.*, heavy nickel plating in build-up and repair work, etc.,—in time the bulk of nickel plating for decorative (and protective) uses will be produced by the employment of bright nickel processes of one kind or another.

TYPES OF BRIGHT NICKEL SOLUTIONS

As indicated above, the two main types of solution employed in this country are (*a*) those based on sulphonic acids—(*e.g.*, Schlötter Electrolyte)—and (*b*) alternatively, those based on cobalt-nickel (the two baths employed here are due to Hinrichsen, and Weisberg and Stoddard respectively).

(*a*) *Sulphonic acid type.*—A typical composition of the sulphonic acid type electrolyte is as follows—(due to M. Schlötter(²)):

	Oz./gal.
Nickel sulphate	27
Nickel benzene-disulphonate	5
Boric acid	5

These quantities are " dissolved in sufficient water to produce a *p*H value of approximately 3·5."

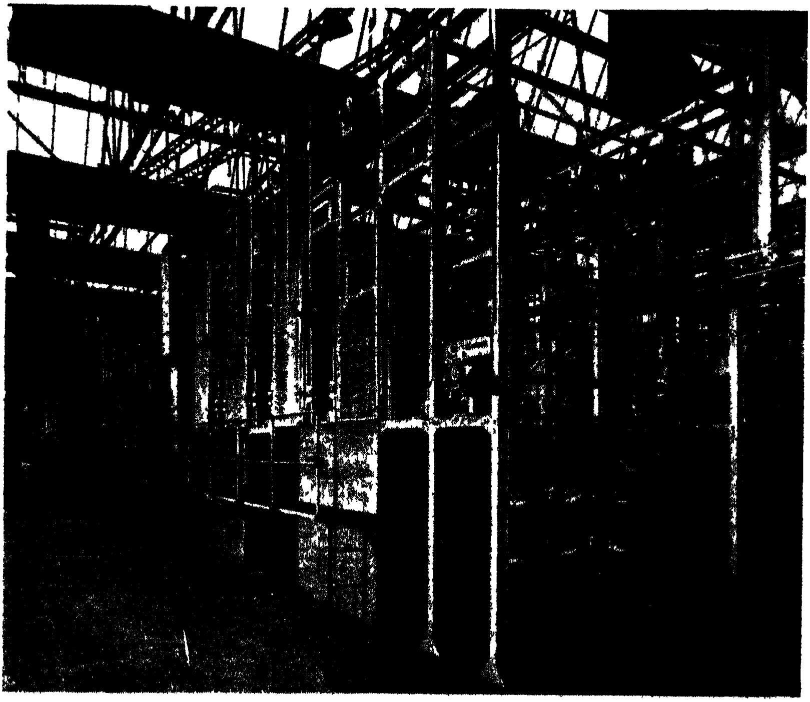
Operating Conditions.—The solution is operated within a *p*H range of 2 to 5, the current densities normally employed being 30 to 50 amps. per sq. ft., although higher current densities are attainable for special purposes. The temperature may vary between 30°C. and 40°C. for the normal current density range. The process necessitates the use of good agitation and filtration, although the patentees recommend that the agitation should not be violent.

(*b*) *Cobalt-nickel Baths.*—Typical of this type of bath is the following solution, due to Hinrichsen:—

	Oz./gal.
Nickel sulphate	40·0
Nickel chloride	7·2
Boric acid	4·8
Sodium formate	6·0
Cobalt sulphate	2·5

The Weisberg and Stoddard bath is similar, except that formaldehyde is employed, which acts as a depolariser.

In this type of bath, the *p*H is kept at around 4 to 4·5, and current densities of the order of 40 to 60 amps. per sq. ft. are readily obtainable, the temperature of the bath being about 130°F. Here again, adequate filtration is essential and plenty of agitation has been found to be beneficial.



[*Courtesy of Joseph Lucas, Ltd., and W. Canning & Co., Ltd.*

Fig. 11.—Automatic bright nickel-plating plant for nickel-plating headlamps (basis-metal—brass)

It should be noted that the deposits obtained in the cobalt-nickel bath are entirely different from those obtained in the sulphonic acid type, in that an alloy of nickel-cobalt is deposited in the former solution, the percentage of cobalt varying, but normally attaining a figure of about 15 to 20 per cent. This necessitates the replenishment of the cobalt in the solution periodically, and the method by which this is carried out differs as between the Hinrichsen and the Weisberg and Stoddard processes respectively. In the latter case, anodes of nickel-cobalt containing approximately 80 per cent. of nickel are employed and cobalt salts are only added to replace drag-out losses. As against this, the Hinrichsen process replenishes the deposited cobalt by direct addition of cobalt sulphate, and this is carried out in direct relationship to the ampère-hour consumption of cobalt in the electrolyte.

DIFFICULTIES CONNECTED WITH THE MAINTENANCE OF FULLY BRIGHT DEPOSITS

While the process of bright nickel deposition has long passed the stage of practical application commercially, it must not be imagined that its operation is therefore free from difficulties. In point of fact, the process, in common with all other technical developments which are improvements on past practice, is necessarily more critical and subject to serious troubles when the operating conditions are not very carefully maintained inside a fairly close range. This can only be countered by increasing vigil in the technical control of the operations, both preparatory to, and during the deposition process itself.

It will be appreciated that where a system is operating in a works which is based on the production of bright nickel, serious difficulties will occur if the standard of brightness is not fully maintained. While this does not necessarily rule out a process in which a reasonable percentage of "rejects" occur, since this can be readily dealt with by the introduction of an inspection stage between the nickel deposition process and whatever subsequent process may be employed, a serious position would undoubtedly arise if the plant suddenly produced either semi-bright nickel or practically dull nickel during the course of working, since this would immediately entail the use of mechanical polishing in order to bring the product up to the desired standard. Since such mechanical polishing "reserves" have either been largely eliminated or turned to other uses as the result of the introduction of bright nickel, the strain on the available plant would be obvious and it might readily reach a point where production was very seriously affected indeed.

Under these conditions it will be readily appreciated that every precaution that can be applied to prevent a diminution in brightness of the finish must be exercised. Practice has indicated that the most important factor which affects the degree of brightness is the freedom from chemical and physical impurities of the electrolyte itself. (It is assumed as a *sin qua non* that the operating conditions —*i.e.*, *p*H, temperature, etc., are all very rigorously and closely controlled so that the process is not adversely affected by lack of elementary attention of this kind.)

Unfortunately, the business of maintaining an electrolyte free from impurities is not an easy one, since impurities may, and do, enter from many sources; as a result, there is in fact a constant battle in progress between the ingress of contaminants and their ejection by special methods. Impurities are obviously entering the solution:——

(*a*) From the atmosphere itself (dust, dirt, metallic particles, etc.) which pervade the average works' atmosphere.

[*Courtesy of New Hudson, Ltd., and W. Canning & Co., Ltd.*

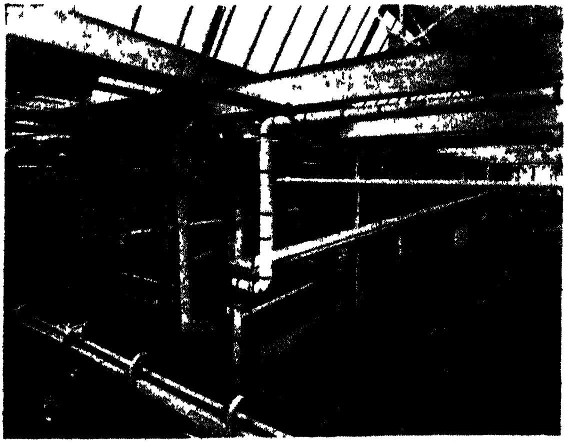
Fig. 12.—Automatic bright nickel- and chrome-plating plant

(*b*) From the articles being plated which, despite preparatory treatment, may still possess a superficial coating of oxide (removed by a slightly acid nickel solution), carbon smut and sludge, abrasive particles such as pumice, lime, etc., which may have been used in the preparatory stages, and finally, the material of the basis metal itself—*i.e.*, iron, copper, zinc, etc.

(*c*) From the anode surface; this may take the form of nickel oxide, carbon and organic impurities from the anode bag material, etc

(*d*) From the material of the plating tank itself, which may contribute a small quota of impurity progressively

As regards metallic impurities, practically all the basic metals entering the solution are deleterious in comparatively small quantity —in particular zinc, copper, iron, and lead. These metals are, however, somewhat selective with respect to the two types of solution. Thus, in the sulphonic acid type electrolyte, copper and lead are particularly deleterious, whereas in the nickel-cobalt processes, zinc and lead most affect the electrolyte. Impurities usually result in a diminution of brightness, particularly on those parts of the articles which are more remote, the effect being greatest at those areas which carry the lowest current densities.



[*Courtesy of Electro-Chemical Engineering Co., Ltd.*

Fig. 13.—Overall view of automatic bright nickel- and chrome-plating plant for steel components, said to be the largest plating plant of its kind built in Europe

METHODS OF DECONTAMINATION OF ELECTROLYTES

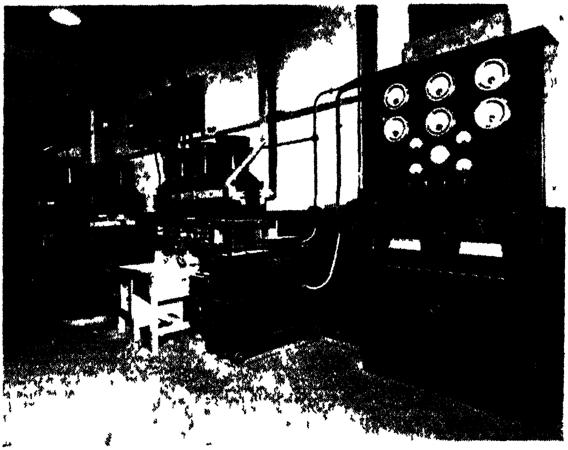
From the above, the paramount importance of filtration is readily apparent, since the employment of a really effective filtration system is one of the most powerful allies in combating loss of brightness in the deposit. However, even with such a system, unless the filtration is of a concentrated type—*i.e.*, is capable of filtering large quantities of the solution in a comparatively small time, there will, nevertheless, be a build-up of impurities which in time will require some special treatment for their removal. One of the most effective correctives is the operation of the bath at very low current density on scrap cathode material. The lower current density results in the preferential precipitation of the contaminants and in time the latter are practically completely removed and the deposit is found to be correspondingly brighter. It may, however, be necessary, where the contamination is very serious, to undertake the wholesale chemical decontamination of the solution. This is carried out most effectively by precipitating by means of nickel carbonate and hydrogen peroxide; the *p*H is thereby raised and the precipitate removed, the solution being filtered back into the tank which has first been thoroughly cleaned out, and thereafter the *p*H lowered to the requisite figure by addition of the necessary amount of acid. The peroxide helps the action by oxidising any iron present to the ferric state and it is precipitated in this condition.

BRIGHT NICKEL-PLATING ON ZINC

Taking the common base metals—steel, copper, brass and zinc—which are normally used in the manufacture of most metal components, the most difficult of these to bright plate is undoubtedly zinc—which is commonly employed in industry in the form of zinc base die castings. In effect, there is little inherent difficulty in the production of bright nickel on polished brass and copper, and even well polished steel, but due to the fact that there is a comparatively large difference between the solution potentials of nickel and zinc, there is a corresponding tendency for zinc to enter the solution, and its deleterious effect on the brightening process is such that the technique for finishing zinc base die castings differs very appreciably from that employed in treating brass and steel respectively. This effect is so serious that so far as the author is aware, there is no process which has so far successfully deposited bright nickel directly on zinc or its alloys, and invariably the articles have first to be copper-plated, while a special solution has to be used for this purpose. This coppering stage is a very important one, and it is not too much to say that the success of the whole process may readily depend on the efficiency with which it is carried out.

INITIAL COPPER-PLATING OPERATION.

It might have been considered that the brightest finish possible would be obtained on a copper-plated surface which itself was brought up to a high polish prior to nickel deposition. Were this the case, it would entail interrupting the process between the copper and nickel stages and introducing the polishing operation—a procedure which undoubtedly would be highly undesirable, both on account of the time factor and the cost of the additional polishing which would be required. Fortunately, however, it was found that such polishing was, in fact, not essential in order to produce the highest degree of brightness in the subsequent nickel plate. In the author's experience([3]) the brightness or reflectivity of the copper deposit was found to be not nearly so important a factor as the production of a closely-grained, smooth and uniform deposit. To produce such a deposit initially, attempts were made to use various

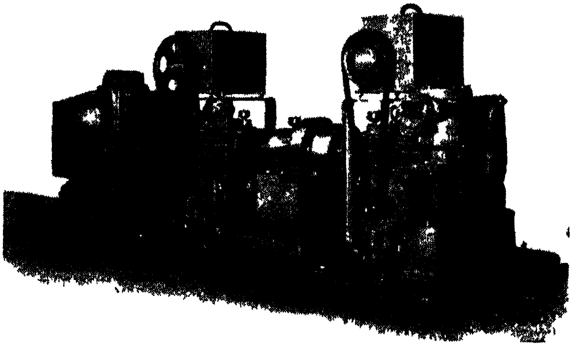


[*Courtesy of Electro-Chemical Engineering Co, Ltd.*

Fig. 14.—Control panel, rectifier and installation for bright nickel chrome plant, showing volt and ammeters, two cleaners, acid etch, nickel-plating and chrome-plating

colloidal addition agents which resulted in bright copper, with the disadvantage that it was usually very distinctly brittle.

An alternative method to brighten the copper deposit is the use of an acid dipping operation after plating, a stage in the process with obvious disadvantages, in particular the proneness of solutions to become contaminated by the dipping acid. Eventually, it was found that the type of copper deposit that was suitable for the purpose could be obtained by using a special electrolyte, which is described below, to produce a deposit ranging from 0·0002 to 0.0003 in., prior to the bright nicked plating operation.



[Courtesy of Electro Chemical Engineering Co , Ltd

Fig. 15—Transfer drive unit used in the plant shown in Fig. 14

PRODUCTION OF COPPER UNDERCOATING

The copper deposition process is based on a cyanide solution which includes a relatively high concentration of Rochelle salts. The following is a typical formula :—

Copper cyanide	3·5 oz.
Sodium carbonate	2·5 oz.
Free cyanide	0·75 to 1·25 oz.
Rochelle salts	6·0 oz.
Water	1 gal.

This solution is operated at much higher current densities than those which are normally employed for ordinary copper plating work. The current density ranges from 60 to 80 amps. per sq. ft. At such current densities there is a tendency for the anode to become polarised and, if this occurs, the anode will not dissolve at its correct rate, resulting in heavy depletion of the copper content of the solution in due course. It is therefore highly important in the control of this process to hold the free cyanide and alkali content as close as possible to that given in the formula. The Rochelle salts help in a very definite manner to stabilise the solution. A very useful check is that of the *p*H of the bath, which should be maintained within the range of 11·6 to 12·3, and for this purpose *p*H indicator papers may be used.

The solution is operated at a somewhat high temperature—*i.e.*, within 140°F. to 160°F.—and here again it is important to keep this factor as constant as possible. Therefore the temperature should be thermostatically controlled.

Under these conditions and at a current density of, say, 60 amps. per sq. ft., the rate of deposition is very high, little difficulty being experienced in producing 0·001 in. of copper within 10 minutes. The speed is such that the timing must be carefully controlled, as every minute results in a deposition of an additional 0·0001 in. of copper. In practice, a stop-clock is a very useful means of controlling the time. There is one disadvantage in this high rate of deposition, in that it results in considerable gas evolution at the cathode, but this can be readily countered by the use of an efficient fume exhaust of the type employed in chromium plating plant.

The copper which is thus deposited will be found, under these conditions, to be of very fine grain, and if not lustrous, to carry a sheen, the fine texture of which is such that bright nickel readily deposits in a highly polished condition forthwith. The work is carefully swilled after copper plating—first in hot then in cold water—and the alkali is neutralised by immersing in weak sulphuric acid, after which the work is again thoroughly swilled and then transferred direct to the bright nickel bath. Needless to say, it is of the highest importance in taking the work from an alkaline to an acid bath that scrupulous cleanliness is observed, and the water changes of the swills must be entirely adequate to ensure that chemicals are completely removed from the surface of the articles which are being treated.

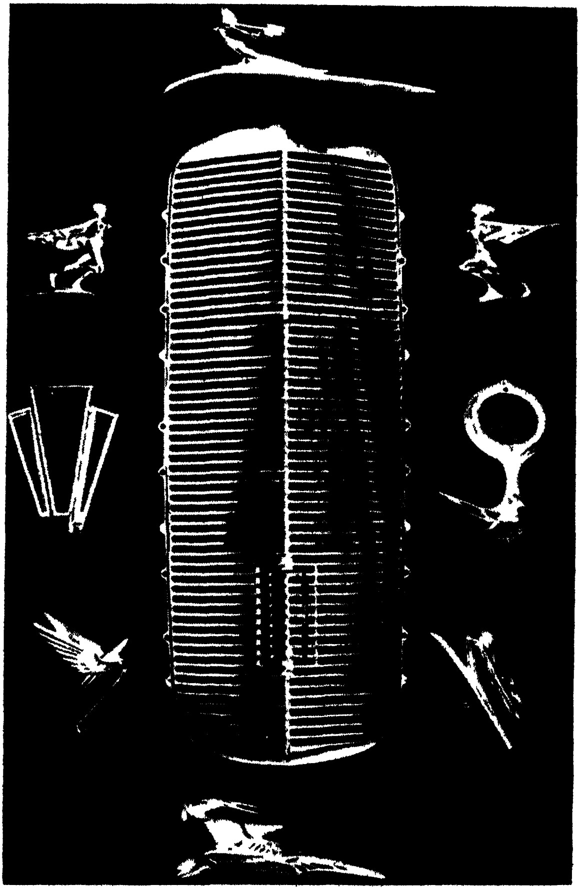
Having produced a sound undercoating of copper, any good well-tried bright nickel solution will then produce a satisfactory nickel deposit. However, the author's experience has been largely gained in the use of the cobalt type of bright nickel bath, and, undoubtedly when this solution works well it produces the requisite degree of lustre to enable the work to pass direct to the chrome vat. It is, however, very sensitive to remarkably small quantities of impurities. This point has already been stressed, but is of even greater importance in dealing with zinc base die-castings than where steel or brass are the base metals. It has been found that while iron is the least deleterious of the contaminants, it is still desirable to keep the concentration of this metal within 0·05 per cent. Zinc, copper and lead, on the other hand, are found to be detrimental when present in as low quantity as 0·002 oz. per gallon (*i.e,* approximately one part per 100,000). It will therefore be appreciated that rigorous steps must be taken to exclude them from the bath, or at any rate to prevent them from building up in the solution to a dangerous degree.

EFFECT OF IMPURITIES IN THE BATH

The presence of these impurities soon becomes discernible, since they result in the appearance of dull patches in those areas of the cathode which receive the least current densities (*i.e.,* in recesses and angles, etc.). Furthermore, the throwing power which is usually very good, is directly affected, while if the quantity of impurity is allowed to rise still further, the brightness of the deposit is gradually affected until it begins to approach a dull condition, and, additionally, its physical properties deteriorate, stress and brittleness becoming apparent. The problem of countering the effects of impurities has been dealt with elsewhere at some length by the author,(4) and it will be opportune to quote from this previous work.

Where contamination has occurred, then the impurities must be eliminated, and one of the simplest and most effective means of doing this is to carry them down as a basic precipitate Precipitation is effected by adding soluble carbonate, preferably that of nickel, but sodium carbonate may be used, until the *p*H of the bath is approximately equal to 5·6/5·8. The precipitate is then allowed to settle, and the solution preferably decanted, the precipitate being then removed. The solution is then carefully filtered and acid added to bring it back to its original *p*H, which, in the case of a nickel cobalt solution is of the order of 4·2/4·4. A variation of this method may be used, in which, in addition to the carbonate, ferrous sulphate is added; experience has, however, shown that this step is not essential

An electrolytic method of removing impurities has been recommended by Weisberg, who suggests that the bath be electrolysed at low-current densities. He recommends current densities of the order of 1 to 2 amp./sq. ft. At these current densities he has found that copper and lead deposit preferentially. Where the contamination is due to zinc, somewhat higher current densities are recommended (*e.g.*, approximately 5 amp./sq.ft.). An obvious advantage of using low-current densities is that there is little loss of nickel (and



[*Courtesy of Wolverhampton Die Casting Co., Ltd.*

Fig. 16.—Bright nickel on zinc base die-castings. Some components presenting difficult features for bright nickel work

cobalt) as a result, since, according to Weisberg, the total current required for the purpose does not usually exceed 5 amp. hours per gallon of solution which is to be purified.

With regard to the nickelling operation, this follows closely the methods which would be adopted in plating brass work. Such methods are quite well known to-day. It is necessary to pay particular attention to the initial cleaning operations and the thorough swilling of articles before they are transferred to the bright nickel tank. Work which is passed direct to chrome plating should preferably be unracked and racked afresh before being placed in the chrome vat. If this procedure is not carried out, then the utmost care must be taken that no nickel solution be introduced in the chrome vat or chromic acid into the nickel vat *via* the racks or jigs.

The nickel solution is best housed in a rubber-lined tank, this type of container having been found to give least trouble, provided the rubber is fully cured. The cobalt-nickel solution is, of course, worked at high-current density (60 amp./sq. ft. to 100 amp./sq. ft.) the solution being air agitated, heated to approximately 140°F. and continuously filtered.

Various types of nickel anodes have been tried; in particular, depassive, cast carbon and electrolytic. The two latter have given good results. Anodes must, of course, be bagged in all cases. Regular analysis of the constituents of the nickel solution and their correction are necessary, and operating conditions must be closely adhered to if satisfactory results are to be obtained.

The greatest difficulty in the production of 100 per cent bright nickel on zinc die-castings (*i.e.*, castings which may be sent direct to chrome without finishing) is the contamination problem It has been found that the shape of the object often determines the percentage of work which will pass through to chrome, articles on which the current density varies to any extent being the most difficult. The possibilities of eliminating *all* nickel finishing are dependent to a considerable degree on the standard of the chromium finish which is aimed at. The full benefit of bright nickel is obtainable on articles requiring a medium or moderately high finish. Under exacting standards of inspection it will be found possible to send at least a proportion of work direct to chrome, while, the remainder, which may be just not bright enough, still presents the advantage that the work may be more easily finished prior to chrome plating than dull nickel would be.

The characteristics of the bright nickel deposit obtained in the manner outlined above have proved to be satisfactory. Apart from the mirror brightness which is obtainable when the process is worked at its highest efficiency, the deposit possesses the following valuable properties:—

(*a*) *Adhesion.*—This property has been found to be of a high order, the deposit standing up perfectly to all forms of mechanical deformation without any sign of the deposit parting from the basis metal. A useful workshop test, which has the advantage of extreme simplicity, is to take occasional small articles from production and deform these severely, observing whether parting takes place at any point on the surface. Satisfactory bright plating resists this rough-and-ready test without difficulty.

(*b*) *Uniformity.*—The bright nickel solution is capable of producing a deposit of reasonable uniformity. The throwing power of the solution is adequate for most purposes, and ordinarily there is little or no difficulty in covering recesses provided these are not too deep.

(*c*) *Freedom from Stress.*—While undoubtedly the bright deposit is more highly stressed than those ordinarily obtainable from dull solutions, it has been found that for all practical purposes this increase is not in any way detrimental. For the majority of applications therefore, the deposit may be considered to be reasonably free from stress, and from observations made to date, unlikely to suffer from the troubles arising from a highly stressed condition.

PROPERTIES OF BRIGHT NICKEL DEPOSITS

There is a striking difference between dull and bright nickel deposits when the microstructures are carefully examined.

The structure of bright nickel coatings is considerably finer than that produced from the ordinary Watts type nickel electrolyte. Often they show an additional curious feature—namely, a number of lines which are more or less parallel to the surface of the base metal. This suggests the operation of a periodic electrochemical effect, the actual cause of which has not been satisfactorily elucidated. It is possible, however, that it may be due to changes in the composition of the electrolyte which may occur periodically in the layer of the electrolyte which is contiguous to the cathode surface. The finer structure is also commonly accompanied by considerable stress. This may be so pronounced that fine hair-lined cracks may become discernible in the surface of the deposit.

As already indicated, the increase in stress does not normally

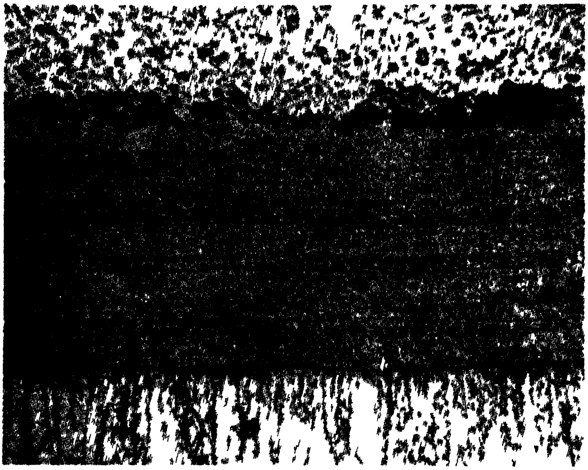


Fig. 17.—Structure of bright nickel deposit Section of etched deposit showing needle structure and " parallel " lines (×100)
(*Reference* J *Electrodepos Tech Soc* 1939, 15, 127)

Fig. 18.—Structure of bright nickel deposit showing " parallel " lines at high magnification (×2,500)
(*Reference.: J. Electrodepos. Tech. Soc.* 1939, 15, 127.)

affect the serviceability of the deposit, but there are obviously certain applications for which the bright deposit would not, on this account, be suitable; for example, on material which is already in a state of considerable stress (*e.g.*, springs), the deposition of bright nickel should be regarded with caution. The stressed condition can be relieved quite considerably by suitable heat treatment.

The physical properties of bright nickel deposit being as stated, it is not surprising that it is much harder than the ordinary dull nickel plate; for example, it may exceed a Diamond Pyramid Hardness number of 500, which is about double that normally found with dull nickel deposits.

Probably the most striking difference between bright nickel and dull nickel deposits is the development and obliteration respectively of the initial degree of lustre of the nickel as it is first deposited. In the case of a dull nickel deposit, normally the initial "flash" is

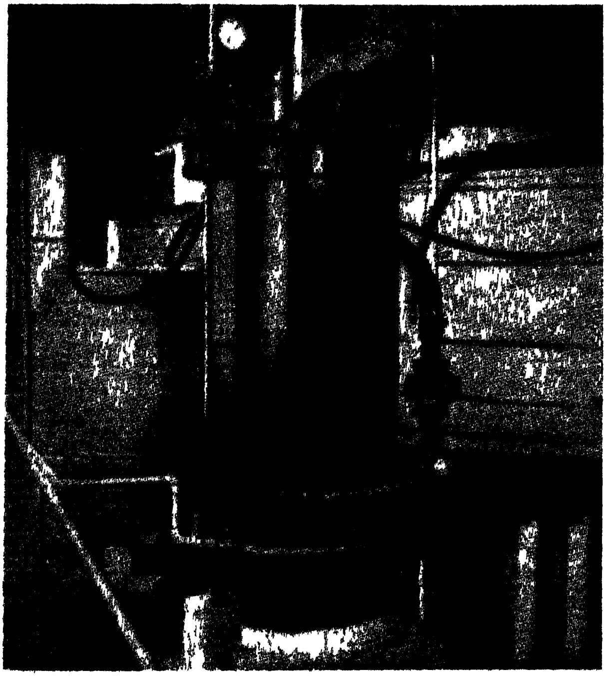


Fig. 19.—Pre-coated filter unit employed in filtering bright nickel solutions
(*Ref.: J. Electrodepos. Tech. Soc.* 1940, 16, 127.)

fairly bright, but as deposition continues it becomes increasingly dull, finally at a thickness of approximately 0·001 in. attaining a matt appearance. On the other hand, the bright nickel deposit increases its lustre progressively during the early stages of normal plating and thereafter remains more or less at this peak until the conclusion of the plating period The actual brightness is, of course,

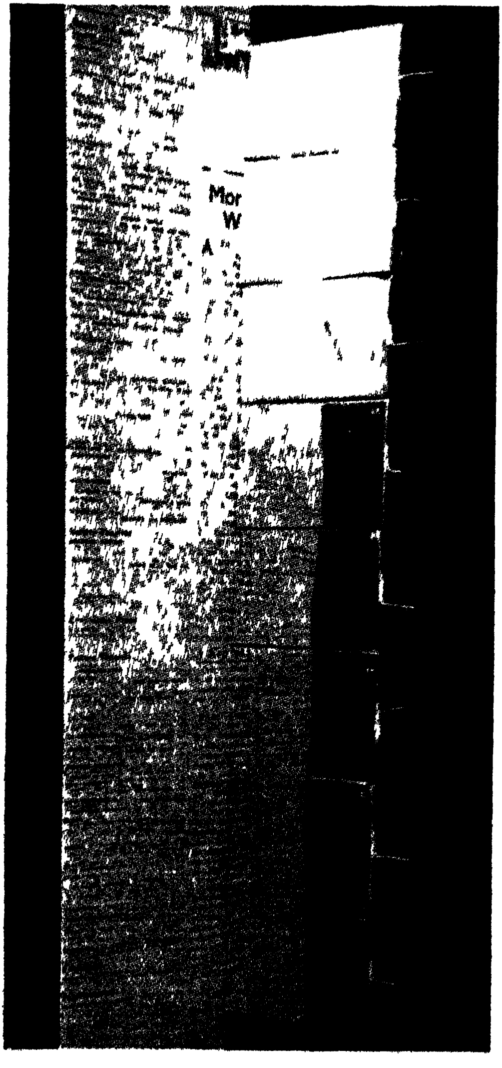


Fig 20.—Effect of thickness of bright nickel deposit on degree of polish attained Progressive increase in thickness results in higher polish

(*Ref J Electrodepos Tech Soc* 1939 **15,** 127)

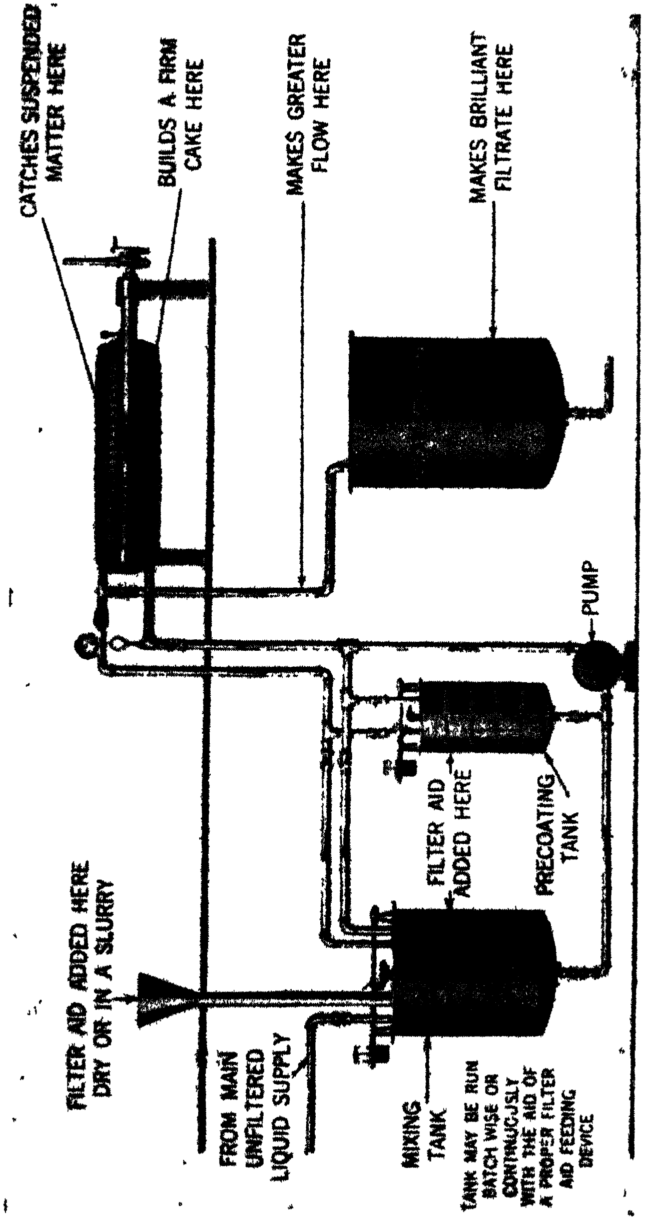


Fig. 21.—General layout of filtration plant employed in filtering a bright nickel electrolyte

(*Ref.: J. Electrodepos. Tech. Soc.* 1940, 16, 99) *dependent on the initial condition of the surface of the basis metal, and the highest degree of lustre is attainable only on a surface which has received a high polish initially.*

The development of bright nickel plating for commercial purposes is gradually reaching the stage where polishing operations will be in the first place considerably reduced, and later on possibly completely eliminated. The ideal is undoubtedly to produce initially a component the surface of which is as highly polished as possible. This polish need not necessarily be produced by mechanical means, but may be attained either—(*a*) by electrolytic polishing methods, or (*b*) by casting in a die which itself has a high polish and imparts this to the casting. The latter is particularly feasible in the case of low-melting basic material (*e.g.*, zinc base die-castings).

Having thus produced as highly finished a surface as possible, the component may then be successively copper-plated, nickel-plated and chrome-plated without any mechanical polishing whatever at any stage. It should be emphasised that this is the ideal rather than the reality of the present, but development has reached the stage where the reality is well within view.

The problems involved in the production of direct bright nickel-and-chrome on zinc base die-castings resulting in a composite deposit of the highest technical quality and finish excellence may, in short, be considered to be well on the way to solution

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(2) M. Schlötter, U.S. Patent 1,972,693 (1934).
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CHAPTER IV.

Electrolytic Polishing of Nickel

ELECTROLYTIC processes for producing a polish on a nickel surface may be divided into two classes (*a*) those producing bright nickel plating, and (*b*) those transforming a dull nickel surface into a bright one by electrolytic means. While Chapter 3 dealt with the production of a bright electro-deposit of nickel, a considerable amount of work has also been carried out on electrolytic processes which are employed for the purpose of producing a polish on both solid and electrodeposited nickel, which surfaces are initailly in the dull, or matt, condition. Such work is of recent date, and one of the first references in the literature occurs some ten years ago, a process being outlined in a German patent, granted to the Elektrokemiska Aktiebolaget, in 1937(1). Two years later an American patent was brought out by Lindh(2) for brightening nickel surfaces (both solid and coated), the electrolyte consisting of a strong solution of sulphuric acid.

A comprehensive account of anodic polishing of electro-plated nickel was given in 1940(3) by Hothersall and Hammond. They point out that while the introduction of bright nickel plating has very largely offset the nickel polishing operation, there is, nevertheless, a definite field for semi-bright as opposed to fully-bright nickel deposits, since the former may require no more than about a quarter of the amount of finishing which would be necessary on ordinary dull or matt nickel deposits. Semi-bright solutions may be justified on the grounds that they are free from some of the drawbacks of bright nickel solutions, as, for example, the higher cost, the greater difficulty of control, the fact that deposits are more brittle and also that they may possess inferior throwing power, so that despite the very widespread use of bright nickel it is suggested that an alternative method of reducing polishing costs would consist in retaining the ordinary standard nickel solutions, the deposits from which could then be brightened by subsequent treatment in a suitable electrolyte. More recently, the production of semi-bright nickel deposits (which provide a more suitable surface for electrolytic polishing) has proved to be a more favourable starting point. However, Hothersall and Hammond's findings are well worth further consideration.

ELECTRO-POLISHING PROCESS

The process is a relatively simple one, since the component to be treated, after being nickel plated, is attached to the anode bar in a solution containing 73 per cent., by weight, of sulphuric acid. Either lead or, preferably, nickel cathodes are desirable (the lead has a tendency to foul the solution by forming lead sulphate). Normally, a temperature of 30°C. and a current density of 250 amps. per square foot is recommended. The time of treatment is very short and ranges from about ½ to 2½ mins.

The choice of concentration is governed by the fact that it is well above the minimum required to produce the polishing action, while higher concentrations are not so practical owing to the necessity for employing a high voltage across the busbars and correspondingly increasing the time of polishing.

OPERATING CONDITIONS

The optimum current density range is found to be in the neighbourhood of 150 to 300 amps. per square foot, the current density favoured being about 250 amps. per square foot. Actually polishing occurs at all current densities in excess of 20 amps. per sq. foot, but it is found that at low current density there is a tendency for pitting to take place.

As regards temperature, while again the polishing action occurs from 50°F. upwards, the conductivity of the solution is comparatively low, below about 70°F. Other considerations make it desirable to employ a temperature between 70°F. and 105° F., the mean temperature being quite suitable.

As regards the time of treatment, this is dependent upon a number of factors, but normally the requisite period is a very small one, usually not exceeding 2½ mins. The factors which affect the time, apart from the initial surface of the deposited nickel and the electrolyte from which it has been produced, are first, the degree of polish which the basis metal receives initially, and, secondly, the thickness of this deposit.

In repeating this work, the author found that superior results could be obtained by prolonging the time of treatment usually to about twice that suggested above (*i.e.*, somewhere in the region of four to five minutes), the resultant effect being quite markedly better. On the other hand, this procedure necessitates the provision of an adequate thickness of nickel initially.

The type of plant which is required is very similar to that which is employed in the stripping of defective nickel from the basis metal. A lead-lined tank is possibly the most useful container, or, alternatively, the tank might be lined with rubber of a quality which will adequately resist the sulphuric acid electrolyte. The usual provision for exhausting the spray from both the anode and cathode and facilities for cooling the solution should the temperature rise as a result of the high current densities employed, represent useful accessories to the plant.

Hothersall and Hammond, in their paper, point out that comparative measurements of the amount of light reflected at 45 deg., using a photoelectric cell, have proved that anodically polished nickel actually has a higher reflectivity than mechanically polished nickel. This result falls in line with similar findings, in the case both of aluminium(4) and copper.(5) This fact is, of course, of the highest significance, indicating as it does the excellent quality finish which is attainable under the best conditions.

The surface condition of the basis metal is just as important in electrolytic polishing of nickel as it is in the production of bright nickel. In other words, it is essential that as high a finish as possible be imparted to the base before the nickel plating operation in both types of processes. This being so, it is important to watch all stages of the preparatory processes, in particular the etching stage, since should this be overdone the initial polish will suffer to such an extent that it can no longer be recovered in the subsequent electropolishing operation. The authors have pointed out that as regards the type of dull nickel solution which should be employed prior to the electrolytic polishing process, an electrolyte which produces a fine-grained deposit is to be preferred. This is due to the fact that the deposits are smoother, and, furthermore, there is a reduced tendency to the production of a surface fog or "bloom" after chroming.

DEFECTIVE WORK

The uniform production of a polished surface is obviously the ideal, but it is not always achieved in practice. Two defects which are not uncommonly encountered in the electrolytic polishing of nickel consist in the production of—(*a*) pits, and (*b*) " streaks."

The pitting again appears to be of two types, consisting respectively of somewhat largish ringed pits and very fine pits which cover the surface fairly evenly. The former type of pits resemble a pock-marked irregular surface, and they appear to occur when the process is carried out at comparatively low current density, disappearing largely when the amperage is raised. They are said to arise from the presence of small foreign particles adhering to the surface of the anode, or, again, bubbles of gas which attach themselves and similarly interrupt the current locally.

The fine pitting, however, is a much more pernicious defect, which may be difficult to counter readily. The surface looks more or less fly-blown, and as the cause is somewhat obscure a really successful and immediate remedy has yet to be produced. There is a possibility that it may be linked up with the presence of organic matter in the solution. Certainly a similar tendency has been observed in the case of certain types of bright nickel solution, and in such cases decontamination of the solution has been found to be reasonably effective. The degree of objection which one might justifiably raise against finely pitted surfaces is dependent to a con-

(a) (b)

Fig. 22.—Anodic polishing of electroplated nickel.
Nickel plated lamp body. (a) As plated
(b) After anodic polishing.
(*Ref.: J. Electrodepos. Tech. Soc.* 1940, 16, 83)

siderable extent on the type of article and its shape which may tend to hide the defect rather than accentuate. On the other hand, there is reason to believe that on standing in the atmosphere the defect may possibly accelerate the period in which brightness is reduced and the metal finally becomes dull.

A point of some importance which must be carefully considered is how far the electrolytic polishing process affects the protective properties of the nickel deposit, since in this process one is dealing not with a solid component, where removal of a certain amount of surface is relatively unimportant, but with a deposit, the thickness of which may already be not far removed from the minimum necessary for the protection of the plated component. This is obviously the case where an article of complex shape carrying a deep bend or recessed angle has been plated, since the inherent non-uniformity of the nickel deposit will already have resulted in a very thin and probably inadequate quantity of nickel on the areas of the article more remote from the anode The amount of nickel which is removed in the electrolytic polishing operation may be of the order of 10 per cent. to 25 per cent., and by keeping this rough figure in mind on more complex shaped objects, the corresponding additional amount of nickel can be added to the component initially so as to allow for the percentage lost in the polishing operation.

Another important point is the possibility that increased porosity might occur as the result of reduction in the nickel thickness. Tests, however, have shown that there is little to fear under this heading in the case where the basis metal is of good quality, but where this is not so, then it is quite possible for the porosity to increase very considerably, thus greatly reducing the protective qualities of the deposit. Here again, a safety-factor can be introduced by increasing the specified amount of nickel deposited in the plating operation.

MIXED ACID ELECTROLYTE

More recent work on the electrolytic polishing of nickel has been carried out by the Battelle Memorial Institute of America.(6) The electrolyte which they have employed consists of a mixture of phosphoric and sulphuric acids. One of the objects of the use of this electrolyte was to counter the practical difficulties which arise through the increase in concentration of dissolved nickel in the solution. The amount which can so dissolve is as high as 4 per cent.

by weight, despite the fact that the saturation point is only about 1½ per cent. The excess over the saturation amount precipitates when the solution is heated, so that nickel sulphate precipitates on the hot surfaces, *e.g.*, heating coils in the bath, thus increasing the tank voltage and decreasing the heating efficiency. It is thus undesirable to employ a high temperature as one of the conditions of operation of this process. It is of course possible to recondition the the solution by deliberately heating it to a high temperature so as to precipitate the nickel sulphate periodically, but obviously frequent correction in this manner would be decidedly disadvantageous on a production basis.

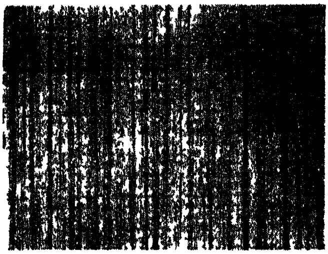

Fig 23—Defects in anodic polishing on nickel
The surface shows streaking
(*Ref J Electrodepos Tech Soc* 1940, 16, 88)

To obviate this, and to make continuous operation of the bath possible without progressive rise in the operating voltage, the solution employed comprises, in addition to sulphuric and phosphoric acids, a small amount of trivalent aluminium (of the order of 0·5 per cent. to 2·5 per cent.). The latter does not merely counter the practical difficulty arising from precipitated sulphate, but is also stated to prevent pitting of the treated surface. Trivalent chromium, which may also be used, is said to have a similar effect.

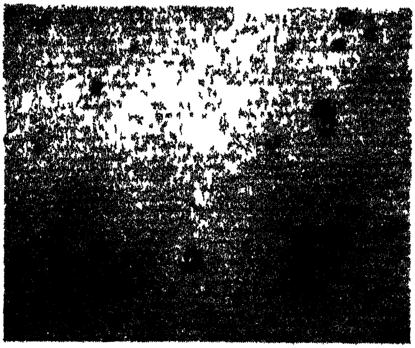

Fig. 24.—Defects in anodic polishing on nickel
Pitting of an annular type
(*Ref . J. Electrodepos Tech Soc.* 1940, 16, 88)

Under these conditions it is possible to reduce the temperature of operation considerably and still obtain a high polish. For example, a bath containing 15 per cent. of sulphuric acid and 63 per cent. of phosphoric acid, the balance being water, makes it possible to carry out electro-polishing as between 115°F. and 130°F. When the trivalent aluminium (or this plus trivalent chromium) is added, pitting is eliminated and higher temperatures may now be employed at lower current densities than those which would normally be required. The above formula appears to represent the preferred bath, possessing the most favourable voltage characteristics, although other baths are tabulated which may be operated under alternative conditions.

While the addition of trivalent chromium is not absolutely necessary, best results are obtained when it is used in association with trivalent aluminium, which appears to be the more important agent of the two salts.

The following two baths are given as being readily maintained in good working condition.

	Bath A.	Bath B.
H_2SO_4	14·5%	13% (by weight)
H_3PO_4	60·6	56
Al^{+3}	2·4	2·6
Cr^{+3}	1·3	1·4
Ni^{+2}	0·5–1	0·5–1
Water	Balance	Balance
Operating temperature	175°F.	115° to 130°F.

It is interesting to note that the electrolytes are said to function quite satisfactorily for electro-polishing nickel which contains alloying constituents—provided that these do not materially affect the behaviour of the nickel in the solution.

The work on anodic processes for polishing nickel has not been pursued as intensively as that on stainless steel, but already sufficient has been done to demonstrate that the process may become of considerable industrial importance. Its survival is bound up with the existence of a powerful competitor which is already well established—namely, bright nickel plating, but nevertheless it would appear that there is a field for the process side by side with bright nickel.

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(3) A. W. Hothersall and R. A. F. Hammond, *J. Electrodepos. Tech. Soc.,* 1940, **16**, 83.
(4) A. Ensor, *J. Electrodep. Tech. Soc.* 1942, **18**, 13.
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CHAPTER V.

Electrolytic Polishing of Aluminium

A CONSIDERABLE amount of development and research work has been carried out on aluminium, and some of the most interesting of this work has centred round the anodic treatment of the surface for more than one purpose. The increasing use of aluminium and its alloys in industry constitutes one of the most spectacular advances in metallurgical progress, and even in pre-war years something like 30 to 40 times the amount of aluminium was being used compared with the total amount produced just over a quarter of a century previously. This arose through considerable improvement in the tensile and general mechanical properties of aluminium when alloyed with various constituents, the obvious advantages of lightness and strength enhancing its value considerably for engineering, structural and similar purposes.

Parallel with this remarkable advance, the revolutionary method of protecting the surface electrolytically by anodic oxidation has steadily progressed, so that in addition to the other important properties of aluminium, its most vulnerable quality, *i.e.*, proneness to corrosion under humid, and especially marine, conditions, has been fully corrected by the effective provision of an artificially produced oxide layer on its surface. This method, in fact, merely considerably strengthens and reinforces the natural oxide film which forms on aluminium when exposed to air, and to which it owes such immunity from corrosion as it initially possesses—an interesting example, incidentally, of an immense improvement on nature by purely artificial means.

The use of an anodic electrolytic process, carrying very high technological significance, is thus not new to aluminium, and in point of fact, so important and widespread has this process become that the term " anodic oxidation " or " anodising " has not unnaturally, but nevertheless undesirably, become synonymous with the surface treatment of aluminium for its protection.

In electrolytic polishing processes, we are also very largely concerned with the phenomena which occur at the anode surface, and it is a moot point how far the processes of anodic oxidation of aluminium have in fact trespassed into the field of electrolytic polishing. More than one process, however, has been developed, and is in successful commercial application to-day, the positive objective of which is the production of a highly polished or highly reflecting aluminium surface. In this country, the most important process of this kind is known as the " Brytal " method, while in America the corresponding process (utilising an alternative electrolyte) is called the " Alzac " process. These will be described in some detail below.

REFLECTING QUALITIES

It is important to appreciate that it is not necessarily the production of the highest degree of polish on an aluminium surface which is likely to produce the best reflecting properties, since a metal reflector may be more valued for the degree of diffusion of light which it produces than for its percentage reflectivity. As has been pointed out by N. D. Pullen, there are essential differences in the requirements of a reflector as against those of a mirror, where the highest degree of polish is desirable. This latter produces the maximum of reflectivity and actually the minimum of diffusion. While reflectivity is highly important with a reflector, in many cases it is the capacity of the reflector to scatter light to the maximum extent which makes it most effective in use.

The successful production of metallic mirrors is, in turn, closely related to the possibilities of producing a plane or dead-flat surface. Normally, this is very difficult with metals which, even when highly polished, are "flowed " as a result of the production of the Beilby layer and are therefore by no means plane. However, mirrors possessing high scattering power (which enables them to diffuse well) are those which are of greatest industrial value, and it is thus possible to make use of surfaces which have been mechanically worked—*e.g.*, spun surfaces, or surfaces which have been mechanically polished. The production of true mirror surfaces would normally require special methods, the most promising of which are rolling methods which result in the production, as near as possible, of an absolutely plane surface.

REFLECTIVITY

It is an interesting fact that as not uncommonly happens in electrolytic polishing work, the reflectivity of aluminium suitably processed anodically can appreciably exceed the reflectivity of the same material when polished by mechanical means. In other words, we are now, as a result of electrolytic polishing methods, able to produce aluminium possessing a higher degree of reflectivity than has ever been possible by any other method in the past. The author, some years ago, pointed out that the reflectivity of highly polished aluminium is superior to that of chromium plating.

Some interesting figures were obtained some time ago by A. H. Taylor who determined the reflectivity of aluminium surfaces when subjected to a number of varying surface treatments. The following table reproduces results obtained for the reflectivity of differently treated aluminium surfaces, using light from a tungsten lamp and ultra-violet light respectively.

TABLE III

REFLECTIVITY OF ALUMINIUM SURFACES WITH VARIOUS TREATMENTS

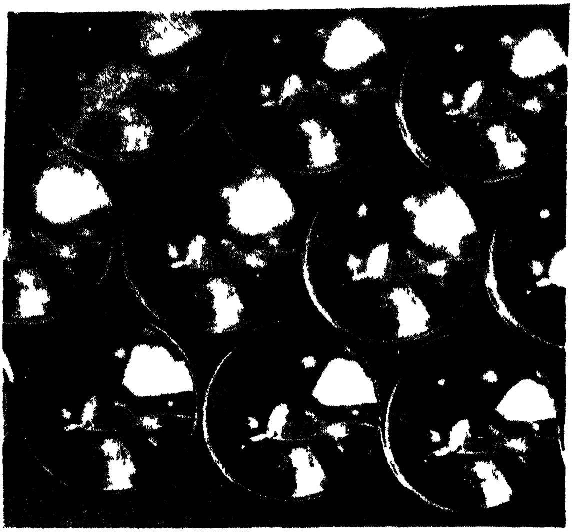
Treatment	Reflectivity per cent.	
	Tungsten lamp (2,000° abs.)	2967A°
1. Rolled	53	33
2. Turned in lathe	83	78
3. Highly polished	72	56
4. Etched or oxidised	75–85	65–82
5. Polished and electrolytically brightened	87	84
6. Polished and electrolytically brightened and anodised in dil. H_2SO_4	85	69

It is interesting to note from the above that the polished and electrolytically brightened surface was superior to all others.

Similar tests were carried out by Taylor, determining the reflectivity for light of a number of different wavelengths in the ultra-violet end of the spectrum

Again, the effect of electrolytic "brightening" is marked. (See Table IV.)

The *modus operandi* of electrolytic polishing of aluminium is similar to that indicated for stainless steel and nickel, but it is possible that there may be border-line cases where there is perhaps a simultaneous electrolytic polishing action as well as electrolytic etching, such as always occurs in anodic oxidation of aluminium. The latter process is a complex one, for in addition to the electrolytic etching action, there is the steady formation and continued growth of the oxide film. This has been fully described, the film growing inwards at the expense of the metal surface, although even this process does not proceed uninterruptedly. Simultaneously with the production of the oxide film, there is also the chemical action on the



(Courtesy of British Aluminium Co., Ltd.)

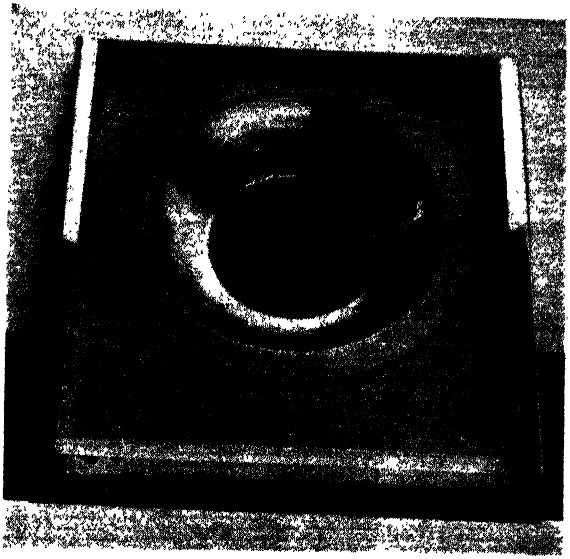
Fig. 25.—Aluminium reflectors treated by the "Brytal" process

TABLE IV

REFLECTIVITY OF VARIOUS ALUMINIUM SURFACES FOR DIFFERENT WAVELENGTHS

Treatment.	Reflectivity per cent.			
	3663A°	3130A°	3967A°	2652A°
1. Etched	81	80	80	76
2. Etched and electrolytically brightened	78	77	77	74
3. Polished and electrolytically brightened	87	85	84	83
4. Polished and electrolytically brightened and anodised—H_2SO_4	79	74	69	62

oxide surface exposed to the electrolyte which results in steady solution of these upper oxide layers. The growth of oxide film is therefore countered by its concomitant dissolution in the electrolyte,



[*Courtesy of British Aluminium Co., Ltd*

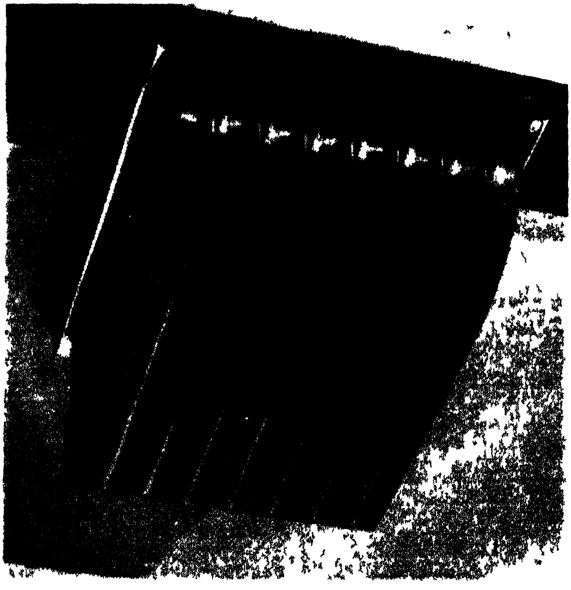
Fig. 26.—" Brytal " reflectors by Benjamin Electric Ltd., in 1939 surface rolling stock of L.P.T.B.

so that if the process is continued beyond the normal specified time, considerable etching of the upper surface takes place. This becomes very evident when the film is dried, since the upper layers are loose and powdery and can be readily rubbed away from that part of the film which adheres to the metal base.

However, although the process is thus complex, it is possible to adjust the conditions of electrolysis, stabilising them at a point where the anodic oxide film formation takes place, while at the same time there is some degree of brightening, and the net result is not a highly polished surface but a degree of lustre, which for some commercial purposes is entirely adequate. Such a surface finish may be obtained when sulphuric acid is primarily used as an electrolyte, and preferably pure aluminium is used as the anode. The finish produced is very characteristic and has been variously termed "satin silver," "translucent," "metallic," etc., all indicative of the lustre of the surface.

While conditions may be so adjusted in other anodising systems —*e.g.*, the Bengough Stuart process (electrolyte chromic acid) and the Eloxal process (electrolyte oxalic acid)—to produce a lustrous anodic film, that obtained from the sulphuric acid electrolyte probably achieves the highest degree of lustre. This is due to the fact that the Bengough process, when carried out as specified, results ultimately in an opaque light-grey finish, while again the Eloxal process produces an opaque finish which tends towards a yellowish-brown tint. On the other hand, the sulphuric acid process naturally results in a translucent finish, tending towards greyness, if the specified time is exceeded in the bath.

The conditions which result in the bright or translucent type of finish in the sulphuric acid process are given below, as they are of most interest in this connection.



[*Courtesy of British Aluminium Co., Ltd*

Fig. 27.—Close-up of lighting fittings incorporating "Brytal" reflectors by Benjamin Electric Ltd. in 1939 surface rolling stock, L.P.T.B.

THEORY OF ANODIC OXIDATION OF ALUMINIUM

The manner in which alteration in the electrical and/or chemical conditions in the electrolyte affects the characteristics of the anode film which is formed is somewhat complex, but an insight may be gained into the mechanism of the process if the theory underlying the formation of the oxide film is given some consideration, and the high lights of the theory are accordingly dealt with below.

It is established that the film consists essentially of Al_2O_3, whatever be the nature of the electrolyte and that the alumina does not exist as such but is to a greater or less extent hydrated. As to the degree of hydration, this is largely governed by the specific conditions which may obtain at the anode interface. These conditions are in all probability quite different from those which exist in the body of the electrolyte; even the *p*H may be quite different, and this despite the fact that all the well-known anodising solutions employed in commerce are highly acid; this arises from the fact that the *p*H in the immediate vicinity of the anode is considerably higher than that in the body of the electrolyte, due to the fact that there is continuous local depletion of acid and corresponding increase in the aluminium content at the anode surface. Aluminium being amphoteric by nature, it is probable that the increase in *p*H will result in hydrolysis and so form a certain amount of aluminium hydroxide.

The author has dealt with the interesting possibilities which are opened up as a result of the formation of aluminium hydroxide in the anode vicinity, in an earlier publication. Briefly, due to the colloidal nature of the hydroxide at the surface layer, it may be expected that both colloidal and electro-osmotic effects arise locally. The film as it forms is itself highly adsorptive. The hydrate in its immediate neighbourhood is probably agglomerated in colloidal form, the colloid possessing a negative charge; there is thus in existence more than one directive factor tending to result in the peptisation of the gel-like hydrate and to impress it upon the anode.

The peptised gel, which may be considered to form a close net-like sponge over the whole anode surface, possesses properties common to such a state of aggregation of matter, and electro-osmosis, or kataphoresis, sets in, resulting in the expulsion of the electrolyte. This occurs when the electrolysis is carried out by direct current. If, however, the current is alternated, the charge on the gel varies with the periodicity, and the electrolyte is correspondingly alternately absorbed and ejected from the structure. Incidentally, it has been claimed that this electro-osmotic action results in a strengthening of the film due to the structure becoming more tough and compact rather in the manner in which a steel structure is strengthened by forging. The author is, however, not convinced that this is the net outcome, as a.c. processes involve intermittent accelerated solution of the surface when the latter becomes the cathode, and this effect is definitely a weakening one, offsetting the " compacting " or hammering effect. In addition, the rate of film formation is retarded, and relatively thin films are ordinarily obtained when a.c. is used.

With regard to the physical structure of the oxide film more recently a special technique has been developed by J. D. Edwards and F. Keller to reveal the structure of cross-sections of oxide films. The method consists in impregnating the porous oxide coating with potassium dichromate immediately preceding the preparation of the polished cross-section, and this is followed by normal etching in 0·5 per cent hydrofluoric acid solution. Examination then reveals that the films consist of two layers. The upper layer is dark and has no visible structure, while the lower layer (*i.e,* that next to the basis metal) appears to consist of alternate dark and light bands, which are normal to the base metal. Near the oxide metal interface, a darker band may be seen, below which there is a delicate tracery, this being the part of the oxide most recently formed on the basis metal.

The dark bands are said to represent the pores which are the connecting link between the electrolyte and the metal base, as a result of which it is possible for the film to grow. According to Edwards and Keller, the oxide layer near the surface of the metal appears to have a cellular structure composed of walls of oxide surrounding the pores or, as is more likely, groups of pores. The structure of the oxide near the surface of the film, however, has been altered somewhat by the solvent action of the electrolyte, and partial solution of the walls of the oxide tubes has produced a sponge-like structure.

FACTORS AFFECTING PROPERTIES OF FILM

The intensity of the reaction and the rate of formation of the film at a given voltage may be very markedly modified by setting up conditions which directly affect the phenomena at the anode/electrolyte interface. By the deliberate addition of certain compounds in the electrolyte, possessing, for example, colloidal properties, not only may the electro-chemical properties of the electrolyte be altered but profound differences in the nature of the oxide film which it produces may ensue. As a result, almost every property of the film may be affected, including its appearance, compactness, hardness, corrosion resistance, electrical insulation, and adsorptive qualites. As a consequence, it is possible from one electrolyte to obtain a glass-hard, compact, brittle, but relatively non-adsorptive oxide film, and from another type of electrolyte, a medium-hard, relatively "spongy," quite ductile and highly adsorptive film.

In general, additon agents of an organic nature produce the latter type of oxide film. For example, addition of glycerine to a sulphuric acid electrolyte very markedly affects the film produced, having the effect of "softening" it to a considerable degree.

The type of film which is, however, required to produce a lustrous finish is obtainable from an electrolyte which is preferably free from addition agents which interfere with the production of a closely grained, glass-hard oxide layer. Thus, an electrolyte consisting of sulphuric acid alone may be employed for this purpose, and the conditions of electrolysis may be readily set down in that they must be such that they do not attack the film once formed to any appreciable extent, since otherwise the surface will be broken up and the reflectivity correspondingly affected. These conditions cover in the main: (1) the composition of the electrolyte, (2) the temperature of the solution, (3) the time of electrolysis, (4) the current density.

(1) *Electrolyte Composition.*—Since the more concentrated the sulphuric acid solution, the greater its etching power with resultant breakdown in the film as formed initially, a relatively dilute solution is best employed. Concentration of the order of 10 per cent. is found to be satisfactory.

(2) *Temperature of the Solution.*—Here again, any tendency for the temperature of the electrolyte to rise will result in surface attack, so that it is essential to maintain the temperature constant—especially as far as possible in the vicinity of the anode surface. Since the solution has a tendency to rise in temperature as a result of the electrolytic action, the solution will require to be cooled artificially—*e.g.*, by means of lead cooling coils present in the solu-

tion, or air agitation, or preferably both. The temperature should be maintained within a range of 75°F. to 80°F.

(3) *Time of Electrolysis.*—As regards time, this must be reduced to a minimum, since excessive contact with the electrolyte will again result in superficial attack. Normally, a process time of 5 to 10 minutes is sufficient to produce the desired effect. This may be reduced somewhat, but the fact that there will be a corresponding sacrifice in the degree of corrosion obtainable must be kept in mind.

(4) *Current Density.*—For sulphuric acid of the above concentration, a current density of the order of 8 to 10 amps. per sq. ft. will be found necessary.

SEALING OPERATION

The anodic film, immediately after formation, is adsorptive and in this condition will take up dye-stuffs, oils, grease, and in fact almost any matter present in a liquid medium with which it comes into contact. After a time, the adsorptive property falls off appreciably, but in any case it is best to "seal" the film to prevent it from absorbing anything further, while, additionally, this also increases its corrosion resistance and renders it more or less stainless. This probably arises through the change in the state of the aluminium oxide from an amorphous to a crystalline condition.

The simplest and most effective method of sealing is to immerse the anodised component, after thoroughly rinsing in clean cold running water, in a tank containing clean boiling water for a period of about half an hour. An alternative method, consisting in immersing the article in a boiling solution of potassium dichromate, increases the corrosion resistance but results in the film developing a yellow appearance.

ELECTROLYTIC POLISHING

The processes outlined above entail anodic oxidation of the aluminium surface, together with a brightening effect. Processes have, however, been developed in which the electrolyte has the true electrolytic polishing effect, comparable in every way with those which have been developed in the case of the stainless steels, etc.

This has been well brought out by Schmitt, who has proved that the effect is one of surface smoothing, resulting in increased lustre, quite irrespective of the treatment which the surface has received before being processed electrolytically. The surface under microscopic examination is shown to have undergone polishing or smoothing even though, initially, it may have been quite rough—e.g., as a result of emery, sandblasting or pickling. In the case of emery treatment, the channels resulting on the surface have shown a rounding of the edges, while in the case of the casting a similar smoothing effect was observed. While the channels or furrows in the emeried surface had not been completely eliminated, they have obviously been very considerably smoothed and flattened. This effect is fundamentally different from etching, since the chemical effect of an alkaline solution on an aluminium surface results in the production of small craters, while if the surface has been emeried then the channels or furrows remain fundamentally unaltered in feature.

BRYTAL PROCESS

While one of the earliest specific references to electrolytic polishing of aluminium was in fact made by Jacquet, in 1937, who used his well-known perchloric acid—acetic anhydride electrolyte, the processes which have become established commercially employ alkaline electrolytes. This is a distinct departure from electrolytic polishing processes which have been considered hitherto, all of which employ acid electrolytes. It is probably bound up with the fact that aluminium is amphoteric by nature, so that it is attacked both by alkalies and acids.

The Brytal process, which was described some years ago by N. D. Pullen and more recently by A. Ensor, consists essentially of a two-stage anodic treatment using direct current. The first stage is the brightening process—*i.e.*, the anodic treatment in an alkaline electrolyte to produce a very thin transparent film and at the same time improve the surface of the metal. The second anodic treatment in an acid electrolyte reinforces the first film without impairing its brightness and this top film can be sealed or dyed.

The first treatment employs a solution containing sodium carbonate and trisodium phosphate. Temperatures of the order of 165°F. to 190°F. are employed, and an initial current density of 50 to 60 amps. per sq. ft. is necessary. This, however, is not maintained, being reduced after a comparatively short time when the anodic film commences to form to some 25 amps. per sq. ft., the voltage being normally between 12 to 15 at this stage.

The pH of the bath must not fall below 10 to 10·5, and as there is a tendency for it to drop, this is corrected by alkali addition—*e.g.*, ammonia, or by hydroxylamine.

The time for treatment is short and normally 5 to 8 minutes, approximately, is all that is necessary, this depending in turn on the composition of the material which is employed. The articles are then removed and rinsed rapidly in clean cold running water, since otherwise the electrolyte, if allowed to remain, would attack the thin film which has been formed by this initial brightening or polishing process.

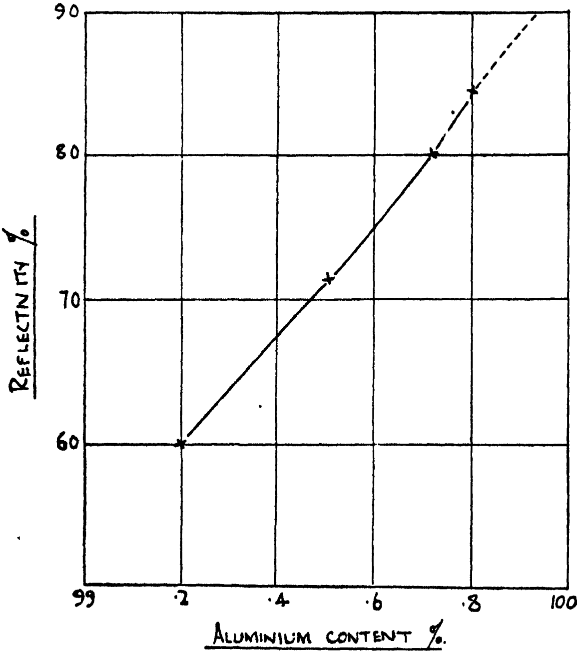


Fig. 28.—Effect of purity of metal on degree of polish obtained

For reflector work, the surface should first have been highly polished, while the brightening effect will be all the more pronounced the greater the degree of purity of the basis metal. The effect of purity of the base metal is quite marked, even in the range of material obtainable between 99 and 100 per cent. of aluminium. For example, in the case of three grades of material containing respectively 99·0 per cent., 99·8 per cent., and 99·98 per cent of aluminium, there is a marked increase in the polish which is attainable with the purest of these materials (see Figs. 28, 29 and 30).

It is of course essential that the articles once polished for reflector work shall be free from surface defects, particularly inclusions and rolling marks. This involves very careful handling of the reflectors before they are processed.

A number of distinct operations must follow the electrolytic polishing process outlined above, since the film produced in the electrolytic polishing stage is not self-protecting and must therefore be reinforced by an anodic operation. In the Brytal process this is carried out as follows:—

The anodising electrolyte consists of a 25 per cent. solution of sodium bisulphate, the anodic effect produced resulting in negligible etching of the surface, so that its brightness is maintained provided that the conditions of operation, especially temperature and current density, are very carefully controlled. A line voltage of about 12 produces a current density of approximately 6 to 8 amps. per sq. ft., and the time of treatment in this bath is some 20 to 30 minutes, the articles being thereafter swilled in cold water and then sealed by immersion in hot distilled water for some 15 to 20 minutes, the temperature of the water being maintained at 180°F. to 185°F. When the surface of the article is examined at this stage, it is found to be covered with a very thin non-translucent film, and this is now removed by immersing the article in a 10 per cent. sulphuric acid bath for a few minutes at room temperature. Thereafter the article is rinsed in cold and then hot water and dried. In order to preserve the finish, the surface is usually covered with a thin film of wax as a final treatment.

LIFE OF ELECTROLYTE

The electrolyte conditions in the polishing process must be adhered to as closely as possible. Nevertheless, there will occur a gradual change in the electrolyte, the solution composition of which will alter with age resulting in a tendency for the current density to fall. In order, therefore, to maintain the current, it is found necessary to maintain the temperature at a somewhat higher point than is the case initially. If the solution be very heavily worked, it is usually found necessary to add both carbonate and tri-sodium phosphate at fairly frequent intervals. As with most electropolishing processes, however, despite all these adjustments it is found that the brightening effect gradually falls off as time goes on and the stage is reached when it is considered that the solution cannot be further corrected and is best discarded. Although it may thus appear that the process requires very careful inspection and control throughout its life, it has nevertheless proved to be entirely practicable industrially and its application has increased very considerably since its initial development, its special field being the treatment of lamp reflectors and searchlight equipment.

ALZAC PROCESS

The Alzac process, which makes use of fluoborates in the electrolyte, has been briefly described as follows.

As with the Brytal process, the final finish of the reflector is dependent very considerably on the quality of the initial polishing, the ideal being a light clean coat which is quite uniform. If the polish is uneven, or if excess pressure creates local burning or smearing of the aluminium surface, a patchy reflector will result. In practice it has been found that the polishing operation is the most vital stage in the whole process, and recent modifications of the Alzac process have been made with a view to reducing the hand polishing operations to a minimum. Actually, the ideal surface for the Alzac finish would not be polished at all, but would leave the spinning or pressing operation sufficiently bright to proceed direct to the electro-polishing solution.

The diffused surfaces are prepared by chemical etching. The electro-polishing solution is contained in a rubber-lined tank in which copper cooling coils serve as a cathode. The process control is designed with a view to maintaining an even and undisturbed polarisation film throughout. Temperature and current density are therefore carefully controlled and the solution is not agitated while work is in the vat. In this respect the Alzac process practice is similar to that employed in the Brytal process, where agitation of the solution is considered necessary only to maintain uniformity but is never carried out when there is any work in the bath and thus only between batches of work. In the Alzac process, as an added safeguard, the copper cathodes are screened with flannel to ensure that gas evolution from them will not disturb the solution near the anode.

Fig. 29 Untreated Super purity 99·98 per cent aluminium reflectors after electro-polishing

(A) 99·8 per cent. Al. (B) 99·98 per cent Al

Fig. 30.—Aluminium reflectors after electro-polishing

The Alzac process produces brightening in about 10 to 15 mins. —*i.e.*, a somewhat longer time than is normally employed in the Brytal process. The aluminium surface when removed from the electrolyte is covered with a polarised film, which is then removed by immersion in a hot alkaline solution. The corresponding anodising bath to provide the protection for reflectors treated by the Alzac process is the sulphuric acid solution, instead of a bisulphate solution, and the treatment which the reflectors receive in this solution is more or less standard with ordinary anodising practice in such baths. Finally, the reflectors are sealed, the simplest method being by immersion in hot water.

ADVANTAGES OF ELECTROLYTIC POLISHING

The advantages which are conferred by electrolytic polishing of aluminium are fairly apparent, and are particularly important in the production of reflectors. Metal has obvious advantages over glass, provided the surface can be maintained in a more or less permanent condition. This particularly applies to conditions of hard service, such as obtain at the present time.

Highly reflecting surfaces can be produced on other metal surfaces, particularly by applying a deposit of silver, which has exceptionally high reflectivity. The drawback, however, is that this falls off fairly rapidly, especially in humid or chemical atmospheres, due to tarnishing. An attempt to overcome this disadvantage of silver reflectors has been developed along the lines of rhodium plating the silver deposit. Undoubtedly this does confer a degree of permanence to the surface, but the process is costly, rhodium being a precious metal, the cost of which in fact exceeds that of platinum. The fact, therefore, that it is now possible to obtain a reasonably permanent finish on aluminium by electrolytic polishing constitutes a definite advance in reflector practice.

Additionally, aluminium possesses the important properties of exceptional lightness and good corrosion resistance as a result of the anodic process to which it is subjected after the electrolytic polishing operation. The surface resists handling and a certain degree of mechanical wear very successfully. It will not tarnish and ordinary chemicals present in the atmosphere have negligible effect on the surface. It also withstands a dusty or sandy atmosphere exceptionally well. The surface is therefore virtually stainless, and it should be entirely unnecessary to clean or polish it, especially with anything which is of an abrasive character. Normally, very light dusting is all that is necessary to maintain the surface, but where this has not been regularly carried out and dirt or soot particles have settled, then a careful sponging with a soap solution, followed by rinsing, will readily restore the original condition and reflectance to the surface.

It has been found that the polished surface stands up remarkably well to elevated temperatures. Thus, according to Pullen, reflectivity in the vicinity of a 1-kw. heating element after 1,500 hours heating resulted in a reduction of only 5 per cent.

Future development in this interesting field may well be concentrated on the perfection of a somewhat simpler process for producing both the required degree of polish and the desired protection in fewer stages than is at present possible. The ideal in fact would be to achieve the desired effect in a single electrolytic operation.

Again, a method of achieving a high degree of polish on surfaces which are (*a*) not so highly polished in the first place, and (*b*) not composed of such highly pure material as is at present necessary, would very much enhance the importance of electrolytic polishing of aluminium. Particularly would this be the case if it were possible to carry out the process on some of the popular aluminium alloys, the position at present being that it is necessary where such alloys have to be used for structural or other reasons to face such material with pure metal before it can be processed.

These are some of the lines along which future development may result in greatly expanding the field of application, which even to-day is already of considerable proportions.

CHAPTER VI.

Bright Zinc and Cadmium Plating

OF the electrolytic processes which result in the production of a bright zinc surface, considerably more interest has been shown in the electrodeposition process, which aims at the production of a deposit of bright zinc rather than in the transformation of a matt or dull zinc surface into one possessing lustre by electrolytic polishing procedure. Indeed, so far, very little may be found in the literature respecting the latter process, although it is somewhat difficult to allocate the precise reason for this state of apparent arrested development. There is no doubt at all that the electrolytic polishing of zinc, and more particularly, zinc alloys, once it is successfully effected on a commercial scale, will prove to be of immense interest to the metal industry, and, in the author's view, there are no insurmountable obstacles which should prevent this goal from being attained eventually, although research work may not lead to an early solution. As with nickel, so with zinc, the production of lustrous effects anodically on zinc surfaces, *e.g.*, on the zinc anodes employed in commercial plating practice, must have been observed by many who come into day-to-day contact with this widely used process.

BRIGHT ZINC PLATING

On the other hand, processes centring round the production of bright zinc deposits have been developed and commercially operated on a considerable scale as a result of intensive research, which has resulted in much technical progress in this field during the last 10 to 15 years. The interest in bright zinc plating is directly connected with the economics entering into the two competing metal finishing processes, cadmium plating as opposed to zinc plating applied primarily for the prevention of corrosion of ferrous material. The advent of cadmium as an industrial finish, which took place some 20 to 25 years ago, resulted in a very considerable demand for this metal and its salts by the electroplating industry—particularly so in the United States, where cadmium was first adopted on a fairly large scale in the late '20s. As a result, this somewhat scarce metal gradually increased in price; but its popularity over its rival, zinc plating, was such that, despite the heavier material costs involved in its production, its sphere of application steadily expanded. The rise in costs was also bound up with the simultaneous increase in the demand for cadmium for use in automobile bearings, and this aggravated the commercial position to the point where eventually the cost of cadmium became a serious factor in the total cost of the finish. At this point, it became highly desirable to produce an alternative to cadmium, the obvious possible basis for which was accordingly the humble, and so far somewhat neglected, zinc-plating process.

CADMIUM *versus* ZINC PLATING

It is pertinent at this juncture to make some observations respecting the comparative protective values of cadmium and zinc plating. As with so many innovations, the cadmium-plated finish was at first adopted with caution by the metal-finishing industry; but enthusiasm increased, and in the author's view, reached much greater heights than is warranted purely on its performance merits. To-day, cadmium plating is widely accepted as a superlative corrosion preventive, and there is widespread belief that it is far superior as a protective of ferrous material than is zinc plating. This, however, is far from being the case, and, indeed, in certain spheres, deposited zinc is the more efficient protective. The enhanced reputation of cadmium has, to a considerable extent, arisen from the results of accelerated corrosion tests, it having been found that its corrosion resistance is particularly high in the well-known salt spray test, for example. While this is so, and establishes a case for cadmium as a useful protective under marine service conditions, it is not superior to zinc plating for ordinary atmospheres, and particularly internal (home or factory) atmospheres.

The enhanced reputation of cadmium is due additionally to its undoubted beauty as a finish, and in this connection zinc plating, which is normally deposited in a matt greyish-white to white finish is not nearly so attractive.

However, the key to the superficial advancement of the zinc finish rests in depositing it in a lustrous form; thus, given an efficient bright zinc-plating process, it is possible to produce a finish which is in no way inferior to the cadmium finish. Such finishes have accordingly been successfully developed and have been put into considerable use in recent years.

BRIGHT ZINC-PLATING PROCESSES.

While most of the electrolytes producing bright zinc are of the cyanide type, more recently solutions have been advocated based on the acid-zinc-sulphate electrolyte. Interesting papers by the Russian authors, N. T. Kudryavtsev and A. A. Nikiforova,(1) indicate that bright zinc plating may be obtained from a weakly acid electrolyte of the following composition :- -

$ZnSO_4\ 7H_2O$	430 grm./litre.
$Al_2(SO_4)_3\ 18H_2O$	30 grm./litre.
$Na_2SO_4\ 10H_2O$	50–150 grm./litre.

To this is added some three to five grams per litre of 2,6- or 2,7-sodium naphthalene disulphonate; while thiourea is another useful addition agent which may be added to the solution.

The *p*H of this solution is maintained at between 4 and 4·5 and the current density employed at a bath temperature which is below 25°C. varies from about 30 to 80 amps. per sq. ft.

The brightening agent does not appear to help the notoriously poor throwing power of the acid-zinc electrolyte, and this is one of the drawbacks of the process.

Most of the cyanide solutions contain the three essential components of this type of electrolyte, namely, zinc cyanide, sodium cyanide and caustic soda, the brightening agent being additional; a wide range of "brighteners" occurring in the literature. The latter, for example, may be one of the colloids commonly employed in brightening deposits, *e.g.*, of the gelatin, dextrin, glucose, etc., class, or complex aromatic or aliphatic organic materials have been specified. For example, a recent patent advocates an aromatic-aliphatic ether containing an aldehyde group.(2) Another (3) suggests the use of a condensation product of a phenol and an aldehyde, together with a soluble compound of one of a number of metals, which include molybdenum, chromium, cobalt, manganese, etc. A further patent (4) utilises as the brightening agent an oxygen containing heterocyclic compound, *e.g.*, piperonal. Another suggests the addition of approximately 0·25 gram per litre of vanillin, veratraldehyde, anisaldehyde, 2,3–dimethyl oxybenzaldehyde, or *o*-methoxy benzaldehyde and a soluble metallic salt, particularly compounds of such metals as molybdenum, chromium, manganese, cobalt, nickel, etc. The range of possible brightening agents thus seems to be extensive.

CHEMICAL CONTROL

While the addition agent is present in relatively small quantity, one of the most essential features in maintaining a bright deposit is the careful control and progressive adjustment of the concentrations of the sodium cyanide, metallic zinc and caustic contents respectively. It is particularly important to maintain a constant ratio of the total sodium cyanide to the metallic zinc, this being a critical factor. The ratio is, in point of fact, comparatively narrow, as has well been brought out in the following table.(5)

TABLE V

EFFECT OF RATIO $M = \frac{\text{TOTAL NaCN}}{\text{Zn (METAL)}}$ ON BRIGHT PLATE

CURRENT DENSITY RANGE AND EFFICIENCY

Ratio M.	Approximate bright plate current density range.		Cathode efficiency at 35 amp./sq. ft. (3·8 amp./dm²) and 85°F. (29°C.).
	Amp./dm.²	Amp./sq. ft.	
2·25	4 to 10	37 to 93	92 per cent.
2·5	2 to 10	18 to 93	88 „
2·7	1 to 10	9 to 93	82 „
3·0	0·5 to 8·0	3·7 to 75	69 „
3·2	0·3 to 8·0	2·8 to 75	54 „

From the above it will be seen that the bright plating current density range is restricted inside a relative ratio of between 2·5 and 2·7 as to total sodium cyanide and metallic zinc respectively present

TABLE VI

OPTIMUM M VALUES *v.* TEMPERATURES

Ratio M optimum.	Temperature.	
	° C.	° F.
2·6 ...	27·8 to 30·6	82 to 87
2·8 ...	31·1 to 33·3	88 to 92
3·0 ...	34·4 to 37·8	93 to 100

in the solution. As this ratio is reduced, higher current densities are necessary in order to obtain the bright-plating range; while as it increases, bright-plating current density range is reduced. Concurrently, also, the cathode efficiency falls off rapidly when the ratio M exceeds 2·7 to 3·0.

Table VI, which is due to the same authors, indicates that the temperature of the bath also has a considerable effect on the ratio which will produce adequate brightness.

While caustic concentration is not so important, the authors have found that a minimum concentration is nevertheless essential, and this is placed at approximately 8 oz. per gallon. Not only does this affect brightness, but also it helps the efficiency.

As for the concentration of metallic zinc, this is not critical, but

[Courtesy of W. Canning & Co Ltd.

Fig. 31.—Bright zinc plating applications

should preferably be inside a range of 4 oz. to 6 oz. per gallon, it being understood that it is maintained in the correct ratio to the total sodium cyanide.

ELECTROLYTIC IMPURITIES.

It may be recalled that one of the prime conditions which it was essential to observe in the production of bright nickel plating was the maintenance of a highly pure electrolyte, comparatively small quantities of impurities, both metallic and organic, being sufficient to affect the current density range of brightness. The first perceptible effects of such impurities, as they build up in the solution, is the production of dull areas in those parts of the surface which receive the lowest current density.

A very similar state of affairs exists in bright zinc plating. Comparatively small concentrations of the heavy metals readily and rapidly affect the brightness of zinc deposits. This is not altogether surprising when, as is well known, the zinc electrolyte is very sensitive to minute quantities of metallic impurity which directly affect the physical properties of the deposit.(6)

Hull and Wernlund recall the belief that molybdenum, which is an efficient inorganic brightener of zinc baths, possibly functions as a result of its property of combining with small amounts of lead, thereby forming a complex compound and so preventing the lead from acting deleteriously.

As the foreign metals build up in the solution and reach a point where they affect the bright-plating range, it becomes necessary to purify the electrolyte. The addition of zinc dust to the solution is found to be effective in most cases, a small amount only being necessary for the purpose (about 0·1 per cent.). After addition of the zinc dust the solution is thoroughly agitated and then filtered before it is again put into use.

An alternative method is to add sodium sulphide, again in about the same concentration as with zinc dust, *i.e.*, about one part per thousand by weight, this resulting in the precipitation of any lead which is present.

Bright zinc plating differs from bright nickel in that the latter requires no further brightening agent when removed from the electrolyte. With some bright zinc-plating processes, the zinc is covered with a surface bloom or film (compare with the Brytal process for brightening aluminium), and this is removed by the use of a suitable dip, *e.g.,* dilute nitric acid. The latter final dip is not, however, uncommon in zinc-plating practice, as some platers make use of such a dip subsequent to dull zinc plating in order to whiten the deposit. (In passing, it should be noted that the belief somewhat popularly held that thereby the surface is rendered tarnish and stain proof cannot be upheld by the facts.)

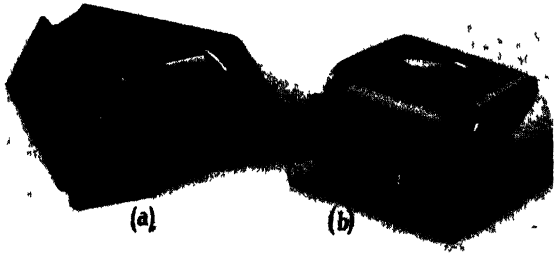


Fig. 32.—Showing at (b) a component which has been bright zinc plated, and (a) similar component which has been dull zinc plated

The alternative possibility of improving brightness is to make use of an electrolytic brightening process; thus, for example, E. Raub and B. Wullhorst (7) claim that not merely zinc but also cadmium and silver may be electrolytically brightened by anodic treatment in a 5 per cent. potassium cyanide solution.

The voltage employed was in the range of 1 to 5 volts; but if the bath is stirred the voltage range for brightening is correspondingly raised. Above 40°C. no brightening takes place, while if more than 5 per cent. of the double zinc potassium cyanide, *i.e.,* $K_2ZN(CN)_4$ or more than 4 per cent. of potash are present, the brightening is affected. Raub and Wullhorst claim that the reflectivity of anodically polished zinc, cadmium (and silver) definitely exceeds that of mechanically polished sheets.

ANODES

Hardly less important than the careful control and maintenance of the bright zinc solution is the purity of the anodes employed. It is obvious that if the latter contain fairly heavy quantities of contaminating metals then these will eventually find their way into the bath and affect the production, and, at first, limit the range of brightness attainable, and, finally, reduce the brightening effect very seriously.

In certain processes, in fact, very highly pure anodes are considered to be essential. As an example, one process specifies a zinc anode containing not more than the following impurities:—

Lead	0·0008 per cent.
Iron	0·0008 per cent.
Cadmium	0·0025 per cent.

It is obvious that the more pure the anode the more expensive it is likely to be, and while high purity is undoubtedly a desirable objective, to specify ultra pure material of the type indicated above rather points to high sensitivity of the bath to such impurities, which must eventually find their way into the solution. It is doubtful, therefore, whether a bath requiring such anodes would possess the necessary flexibility for use under commercial conditions.

An anode which is much favoured, particularly in America, is one to which aluminium is added. It is claimed for this anode that the aluminium is not in any way deleterious; but it has the important characteristic that it prevents undue dissolution of zinc; since the anode efficiency is almost invariably higher than that of the cathode, the anode has in fact a stabilising effect on the electrolyte, rendering control far more simple.

Still a further anode which was at one time recommended was characterised by the addition of mercury. Such an anode was used specifically in a solution which itself contained a certain amount of a mercury salt, some of which found its way over into the electrodeposit, thereby enhancing the lustre. It was further claimed that the use of mercury salts helped the throwing power of the solution and also increased the cathode efficiency. The claim was also made that such a solution was very useful in plating ferrous castings, in particular.

How far these claims can be substantiated is somewhat doubtful; but, in any event, the tendency in the last few years has been to move away from mercury-containing bright zinc solutions, such solutions, in fact, being banned altogether in specifications for zinc-plating service parts, particularly aircraft equipment. This arises from the distinct possibility that amalgamation might take place, resulting in immediate disintegration of aluminium; while in the case of brass, season cracking might also very readily occur.

There are other disadvantages which apply to the mercury type bright zinc solution arising from the fact that the mercury is apt to precipitate out from the electrolyte, it being not uncommon to find mercury at the bottom of the solution. It is also possible for mercury to "sweat" out of the electrodeposit, and sufficient has perhaps been said on this subject to indicate that for most purposes the mercury bright zinc process has several serious drawbacks.

PREPARATION OF THE CATHODE SURFACE

The preparatory treatment of parts for bright zinc plating, while following the normal lines, is to some extent more critical than in the case of work which is destined for dull zinc plating. Normally, it is not uncommon to find that in plating practice much less care is devoted to the cleaning and swilling of parts in the zinc-plating department than is the case in the nickel-plating section. This arises from the fact that lack of care in the preparation of work for nickel plating will very rapidly result in defective plating, *e.g.*, stripping, blistering or pitting may supervene.

In zinc plating, on the other hand, components which are not completely cleaned may nevertheless pass through the plating operation with, at any rate, superficial satisfaction. It is not uncommon, therefore, to find that the cleaning of the surface is desultory and the rinsing of each of the chemicals decidedly sketchy.

This will not do if the objective is bright zinc plating. The intermediate rinsing operations in particular must be carried out very carefully, so that all trace of chemicals, whether acid or alkaline, is removed before the object finally enters the bright zinc electrolyte. One of the greatest economies in the plating shop arises from an apparently costly superabundance of clean cold running water, and it may often be found that this elementary provision (which seems so difficult of attainment in the average plating shop) helps, to a very considerable degree, in solving many of the problems which are often attributed to other causes. In the case of the bright zinc-plating process, where small quantities of impurity will upset the electrolyte, it may even prove desirable to have the incoming water treated, should it be of a "hard" nature. The importance of water of as high purity as possible is one which is likely to become of greater significance, in the near future, in respect of all plating operations—but particularly in the case of such critical processes as the production of bright deposits.

ADVANTAGES OF BRIGHT ZINC PLATING

Apart from the obvious advantage in the added lustre which occurs in bright zinc plating, one or two other properties of the process make it interesting from the point of view of easing production.

In the first place, the solutions are usually capable of being operated at relatively high current density. Current densities of the order of 40 to 100 amps. per sq. ft. are not uncommon, and a current density, say, in the neighbourhood of 45 to 60 amps. per sq. ft. will usually more than double the rate at which zinc can be deposited under normal conditions. Such high rates of deposition are also often possible without any considerable agitation of the solution, and, in fact, where no agitation whatever is employed.

The risk of " burning " or piling up on protruding parts of the work is also considerably reduced, despite the high current density employed, so that it is possible to plate articles of complex shape more readily than is the case in a dull zinc solution. There is also a quite appreciable tendency to increase in the throwing power of the solution, and no doubt this and the fact that burning is reduced are both traceable to the same cause, namely, a rise in the cathode polarisation, which is a fairly common attribute of bright solutions.

One difficulty which does arise from plating work with considerable recesses is due to the fact that the current density may approach the lower end of the bright range in deep recesses of the component. Where this occurs, there may be local solution of the cathode material and as a result the electrolyte may be contaminated. The importance of removing such contamination has already been indicated, and fortunately this can be done quite readily by electrolysis, using scrap cathodes at a somewhat low current density for a period which will vary with the degree of the contamination. At worst, it may be necessary to purify by the sulphide method mentioned above.

ELECTROLYTIC POLISHING OF ZINC

As already indicated, comparatively little has appeared in the literature so far on this aspect of the subject. Apart from Jacquet's work earlier noted in this book, one of the most important contributions has been made by W. H. J. Vernon and E. G. Stroud.(8) The latter authors prepared the zinc surface (using pure zinc for the purpose) by a preliminary abrasion with emery, followed by degreasing in an organic solvent.

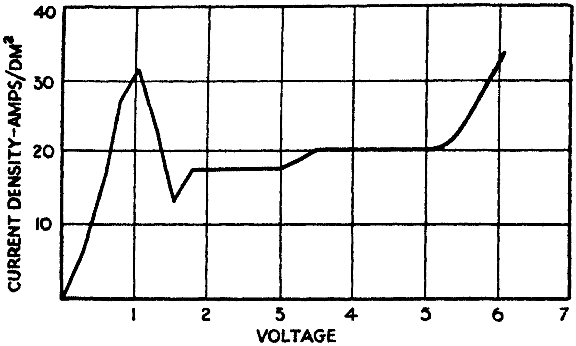


Fig. 33.—Current-voltage curve (electrodes 2·5 mm. apart)

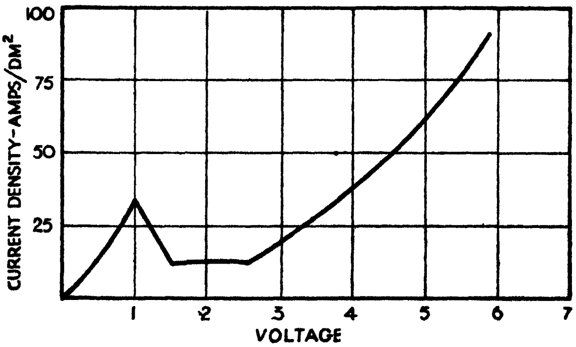


Fig. 34.—Current-voltage curve (electrodes 15 mm. apart)

The electrolyte consisted of a 25 per cent. solution of potassium hydroxide and for the cathode a strip of copper was employed. The solution was worked at room temperature and agitated by the passage of a stream of air or nitrogen. Typical curves showing the relationship between the E.M.F. and current density (Figs. 33 and 34 were obtained. The curve is quite similar to that which is usual in most electrolytic polishing processes. Two curves were actually obtained for electrode distances of 2·5 millimetre and 15 millimetre respectively.

The authors reported that polishing occurred without evolution of gas in the range represented by the nearly horizontal portion of the curve, this being equivalent to a current density of approximately 16 amps. per sq. decimetre. If the E.M.F. was raised or lowered below this value, no polishing occurred, and instead the surface became etched or roughened, gas evolution taking place during the action, but at still higher values, polishing again took place, this time accompanied by gas evolution.

Where the specimens had been originally treated with fine emery paper, *e.g.*, finishing with Hubert 0000 after 15 minutes at 6 volts, excellent polishing results were attained; but the authors record, too, that it is possible to obtain quite satisfactory surfaces, even if the initial surface appearance be rougher, by increasing the time proportionately.

BRIGHT CADMIUM PLATING

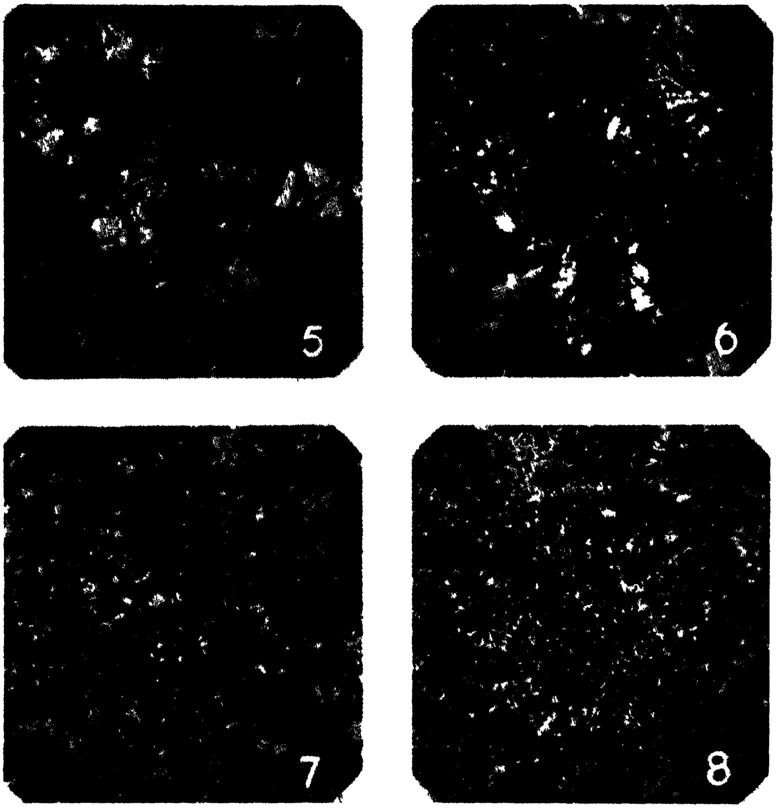
Most of the remarks pertaining to bright zinc plating mentioned above will apply in general to bright cadmium plating. The solutions employed are somewhat similar in character, although a wide variety of electrolytes has in fact been proposed both in the technical and patent literature. A typical solution contains cadmium oxide, sodium cyanide and an addition agent, which is usually organic, but may be inorganic in nature (or a combination thereof may also be employed).

Mathers and Guest (9) have proposed the following solution :—

Cadmium oxide	45 grm. per litre.
Sodium cyanide	120 grm. per litre.
Sodium sulphate	50 grm. per litre.
Addition agent	10–50 grm. per litre.

The addition agent consists of a material known as glycerol "foots." These are residues remaining after the distillation of glycerol in soap manufacture. The quality and composition of the foots varies somewhat with the manufacture, and the concentration which is required is dependent upon the material available, hence the range in concentration that is indicated in the formula. It is interesting to note that pure glycerol alone appears to have little or no brightening action.

The current density which is employed is given as varying from 23 to 42 amps. per sq. ft., and is again dependent on the quality of the addition agent. Normally, room temperature is employed, and a further brightening action is obtained by the use of a rapid 1 per cent. nitric acid dip.



Figs. 35-38.—Cadmium deposits from $CdSO_4$ electrolyte at various pH values showing effect on crystal structure (x350)

A German patent granted to R. Weiner, of the Deutsche Gold-und-Silber-Scheideanstalt Vorm Roessler,(10) claims the production of fully bright cadmium deposits by the use of various inorganic metallic additions in comparatively small quantity, the metals employed varying considerably. Thus, for example, in the molybdenum group, tungsten, chromium and uranium may be employed, the preferred concentration varying between 0·01 to as much as 40 grms. per litre.

In the iron group, cobalt and nickel are included, and the range is much narrower, varying from 0·05 to 1·0 gram per litre. Another group includes titanium, silicon, zirconium, thorium or aluminium. Claims in this patent are distinctly wide and some examination of their practical applicability is probably desirable. To such a solution organic addition agents are also suggested, including heliotropine, safrole or coumarin.

ACID ELECTROLYTE

Very little may be found in the literature on the possibilities of employing an acid cadmium solution for the production of bright deposits in the same way that is possible in bright zinc plating. This is due to the fact that while copper, nickel and zinc are all capable of being deposited from sulphate solutions in a finely crystalline form, cadmium is ordinarily obtained in the form of coarser-grained crystals when deposited from solutions of cadmium sulphate. Actually, however, were it possible to make use of an acid cadmium bath, the advantages would exceed those in bright zinc plating from acid solutions, for not only is it obviously more agreeable to use a sulphate solution, compared with the cyanide electrolyte, but in contrast to the drawback of sulphate solutions in zinc plating as a result of their poor throwing power, the cadmium sulphate electrolyte possesses remarkably good properties in this direction, covering intricate or complex-shaped objects satisfactorily.

The sulphate electrolyte has from time to time been investigated by different workers in the field; thus, as early as 1905, Holtz (11) attempted to deposit cadmium from a sulphate solution, obtaining spongy and " treed " deposits. This experience was also shared by Kohlschutter and Good.(12) A useful study had meantime been contributed by Desch and Vellan,(13) who experimented with a number of electrolytes, including, in addition to the sulphate solution, the chloride, oxalate and fluosilicate, although they were primarily interested in depositing cadmium on aluminium and its alloys. However, they were able to obtain quite promising results by the use of a cadmium sulphate solution which contained ammonium sulphate and peptone as addition agents. Just prior to this, Millian (14) in Belgium, had found that gelatin, when added to a cadmium sulphate solution which contained also sodium sulphate and sulphuric acid, produced a more brilliant deposit, which was also reasonably adherent. Humphries ([15]) used glue as an addition agent and later ([16]) advocated the use of other addition agents, including malted syrup and caramelised sugar.

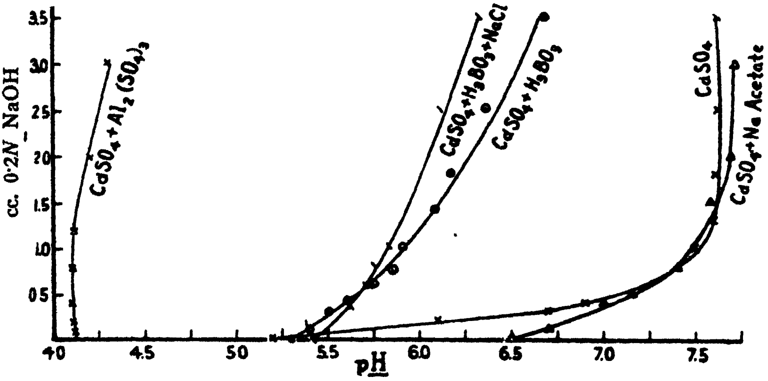


Fig. 39.—Buffering properties of mol. $CdSO_4$ solutions with various added buffers

Some years ago the author ([17]) made a study of the cadmium sulphate electrolyte, investigating, in particular, the effects of a variation in the current density and temperature of the solution on the crystal structure of the grain size of deposit. On the assumption that reduction in the grain size produces a more compact deposit tending towards lustre, this study is of interest in that it indicates somewhat the factors which tend towards grain size reduction of the cadmium deposit.

It was found, for example, that the *p*H of the solution exercised a very marked effect on the structure and crystal size of the deposit. The optimum *p*H appeared to be in the neighbourhood of 5 to 5·7, when a considerably closer-grained deposit was produced than those obtainable at lower *p*H's. (See Figs. 35, 36, 37 and 38). On the other hand, when the *p*H exceeded 6·0 darker granular and less adherent deposits were produced, due possibly to occlusion of oxide or hydroxide. This indicated the necessity for employing a suitable buffer, and aluminium sulphate was found to be the most promising of those investigated. (Fig. 39.) A solution which produced small-grained deposits was accordingly built up after various possible constituents were investigated and selected as follows :—

Cadmium	112 g./litre
Boric acid	30 „
Sodium chloride	6 „

The effect of current density and temperature was studied, it being found that as the current density rises the grain size is reduced. On the other hand, the crystal size is smaller at lower temperatures, up to, say, 50°C. Beyond that, increase in crystal size occurs. Agitation of the solution helps to produce a " structureless " deposit, and addition agents of the type of dextrin, gelatin and peptone resulted in further reduction of crystal size and brightening of the deposit.

It is remarkable that so little work has been done in this field, having regard to the possible promise which is opened up for bright cadmium deposition in acid type electrolytes.

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CHAPTER VII.

Bright Copper Plating

COPPER and silver are akin in many respects, and they are also among the oldest metals to be deposited industrially. It is just over a century ago since the famous patent on silver plating was granted to Elkington. This patent, although constituting one of the earliest publications connected with electrodeposition, contains details of one of the few processes which have not experienced marked alteration or development in the intervening period, silver-plating practice having undergone little change substantially and being closely followed in many silver-plating establishments, which themselves indeed have undergone almost as little change in the operating plant and equipment employed for the purpose. However, very considerable progress has been made within the last ten to twenty years in the elucidation of the phenomena which occur in the deposition of silver, and particularly in the production of bright deposits.

Copper plating, too, is a comparatively ancient practice, the copper sulphate electrolyte, in particular, having been used for very many years. Here, again, considerable progress has been made in the production of bright copper deposits, both from the alkaline and acid electrolytes.

A fair amount of useful work has also been carried out recently in the sphere of electrolytic polishing both of copper and silver. These metals will be dealt with in this and the following chapter.

BRIGHT COPPER PLATING

It has been known for many years that the addition of small quantities of certain materials, mainly of the colloid type, results in the normal matt copper deposit which is obtained from an acid copper bath (containing essentially copper sulphate and sulphuric acid) being converted to a deposit varying in the degree of brightness according to the amounts added and the conditions of deposition obtaining in a given case. The increase in lustre is associated with a corresponding decrease in the grain size of the deposited crystals, it being evident that this occurs as a result of the colloid or other addition agent migrating to the cathode, and there interfering with the growth of individual crystals.

Various theories have been advanced to elucidate the mechanism of this phenomenon, but there can be no question of the fact of interference. Perhaps the most striking evidence of this is the work of Grube and Ruess,(¹) who were able to demonstrate the inclusion of gelatin in the copper deposit obtained from a cyanide copper electrolyte showing that the metallic deposit and gelatin were impressed on the cathode in the form of alternate layers. This formation, however, is not characteristic of all addition agents, since in most cases the addition agent is mingled with the deposit and its precise location not readily traceable. In practically all cases, the addition agent may be found bound up with the deposit, in one physical form or another.

Reference has already been made in an earlier chapter to the refining effect on the copper deposit obtained from a cyanide solution by an addition of Rochelle salt such a finely grained copper deposit being essential on the surface of a zinc base die-casting preparatory to bright nickel plating. The deposit obtained under these conditions is not fully bright, and indeed mirror bright deposits have so far not been achieved, at any rate on a commercial scale, from cyanide type electrolytes, although processes have been described which are said to produce a reasonably good lustre. For example, the following electrolyte is given in a British patent for the production of bright deposits.(²)

Copper Thiocyanate	20	grms./litre
Sodium Cyanide	110	„
Caustic Potash	40	„
Sodium Bicarbonate	10	„
Turkey Red Oil	4	„
β—Naphthol	2	„

Besides the addition agents indicated in the above formula, other suggested colloidal agents are glue, agar-agar, gelatin, bitumen, beechwood, tar, etc.

Many bright copper plating electrolytes have, however, been advocated which are based on the acid copper bath; thus, for example, F. L. Clifton and W. M. Phillips (³) advocate the use of the following solution.

Copper sulphate	210 grms./litre
Sulphuric acid	30 ,,
Molasses	0·80 ,,
Thiourea	0·04 ,,

A further bath (which does not produce such a bright result) advocated by the same authors,(3) is the following :—

Copper sulphate	250 grms./litre
Sulphuric acid	10 ,,
Triton No. 720 (Wetting agent) ...	0·2 ,,
Thiourea	0·01 ,,

(Triton No. 720 is a salt of a sulphonated ether.)

The conditions of operation of the first bath are :—

Current density	70 to 75 amps./sq. ft.
Temperature	21°C.

while for the second bath, they are :—

Current density	48 amps./sq. ft.
Temperature	21° to 27°C.

Vigorous agitation is necessary.

In the latter bath it was found that traces of chloride were apt to reduce the brightness and finally result in its elimination. On the other hand, sodium and magnesium ions helped the production of bright plate, but caused burned deposits to form at high current density. Raising the temperature resulted in reduction in brightness.

In the case of the fully bright bath, the authors found that addition of molasses also decreased the tendency for striation in the areas of low current density.

Very interesting results have been obtained by addition of ammonia and ammonium salts to the copper electrolyte, and various independent authors have formulated processes based on such electrolytes with good results; thus, T. G. Coyle (4) makes use of the following electrolyte.

Copper	28 to 38 grms./litre.
Sodium pyrophosphate ...	150 to 300 ,,

Ammonium hydroxide to produce a *p*H 8·3 to 8·5.

The conditions are :—

Current density	20 to 40 amps./sq. ft.
Temperature	38 to 60°C.

The deposit, which has a satisfactory lustre, may be produced directly on non-ferrous articles (other than zinc). Zinc and steel must first be flash-coppered in a cyanide solution.

Similarly, the Russian authors, O. K. Kudra and G. S. Kleibs (5) have suggested the following solution:

Copper sulphate … … … …	65 grms.
Ammonium sulphate … … … …	20 „
Ammonium hydroxide (25 per cent.) …	500 ml.
Water to … … … … …	1,000 ml.

claiming that the copper may be deposited direct on iron, aluminium and duralumin, and is shiny, dense and adherent.

The current densities advocated on aluminium are of the order of 30 amps./sq. ft., and about 50 amps./sq. ft. on duralumin.

L. Greenspan (6) has been responsible for a very useful investigation on the use of amines in copper plating solutions. Previously, R. H. Atkinson had patented the first of these solutions in 1934.(7) C. J. Brockman (8) and co-workers describe the use of such as the ethanol amines and the ethylene amines in the deposition of copper, obtaining semi-bright plates, which Greenspan showed were invariably brittle. The bright throwing range was also inadequate. By adding ammonia to the solution of these amines, Greenspan found that he was able to eliminate the brittleness. The effect of the ammonia additions was quite significant. With increase in ammonia content, the deposit became increasingly brighter at the high current density areas, but duller at the low c.d. regions. It being thought that this might be due to *p*H variations in the cathode film, the use of a buffer was employed, a suitable buffer being found to be ammonium sulphate. The results appear to have been quite startling, as when this latter salt was added at a concentration of 15 to 20 grms./litre, the deposit became uniformly bright over the entire surface of a bent cathode. Furthermore, the deposit was also completely free from brittleness.

In discussing these results, the author considers that the ammonium sulphate functions as a result of its buffering action, and since it was found that the addition of this salt alone could produce uniformly bright, brittle-free deposits, it was thought that this arose partly through the formation of a certain amount of free ammonia, as a result of ammonium sulphate addition to the copper sulphate electrolyte, containing an amine such as diethylene triamine. The *p*H of the solution was around 9·0 to 9·5, and this value is significant in determining the relative amounts of free and combined ammonia. In practice, it was found necessary to add free ammonia periodically in order to make good losses due to evaporation, drag-out, etc.

Two types of electrolyte were developed, the one containing a high and the other a low metal content, the optimum concentrations being as shown.

High Metal Electrolyte.

Copper sulphate crystals	100 grms.
Diethylene triamine	80 cc.
Ammonium sulphate	20 grms.
Water	1 litre.

Low Metal Electrolyte.

Copper sulphate crystals	50 grms.
Diethylene triamine	45 cc.
Ammonium sulphate	40 grms.
Water	1 litre.

With reduction in the metal content it was found necessary to increase the ammonium sulphate concentration.

Incidentally, it is pointed out that besides the diethylene triamine, other amines may be used, such as triethylene tetramine, tetraethylene pentamine, hydroxyethyl ethylene diamine, etc. The result in all cases was found to be very good.

Possibly the most interesting point about Greenspan's work is that it is not merely a report of laboratory findings, but it is understood that it has been translated into shop practice with very satisfactory results in America. For example, a bath which was installed was functioning well after 18 months' working. So far as practical details are concerned, the solution is agitated by means of cathode bus-bar movement and kept at a temperature of 60°C., being occasionally filtered in order to keep it free from impurities which may be in suspension.

The current density employed is 40 amps./sq. ft. normally, but may rise to as high as over 100 amps./sq. ft. on certain types of components.

With regard to ammonia replacement, which is necessary to maintain brightness and ductility, normally some 3 to 5 cc. per litre of concentrated ammonia is necessary per day, to keep the solution in good order.

Pitting has been encountered, and is believed due to iron impurities, rubber-lined equipment and non-metallic plant generally being therefore helpful factors in preventing accumulation of such undesirable matter.

As in bright nickel plating, it has also been found that certain organic impurities will result in dullness, and as with nickel, too, this may be dealt with by means of activated carbon treatment, filtration, etc. The solution also runs parallel with bright nickel-plating experience in that the addition of a wetting agent, which reduces the surface tension, also helps to eliminate pitting to a considerable extent.

High purity anodes have been found necessary, and rolled electrolytic copper is preferred, the anode current density being kept low and preferably not in excess of 15 amps./sq. ft.

With regard to chemical control, the solution appears to be readily amenable to analytical methods; thus, the total nitrogen, which is an important figure, can be determined by the usual Kjeldahl method, while free and combined ammonia are obtained by distillation, and the total sulphate determined gravimetrically. This provides the necessary data for determination of copper sulphate, ammonium sulphate, free ammonia, and the addition agent, diethylene triamine. Not least of the important applications of a successful bright or semi-bright copper deposition process is its value as an undercoating to bright nickel plating in fine base die castings and aluminium and its alloys.

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CHAPTER VIII.

Bright Silver Plating

ONE of the earliest bright deposits to be produced was probably that obtained from a silver cyanide electrolyte containing an addition of carbon disulphide. The importance of producing a silver deposit which could readily be polished, thus resulting in a bright lustrous finish for silverware, was early realised by craftsmen in the Sheffield district almost from the earliest days of the establishment of the process. It was necessary that the deposit should take a high polish rapidly, not only in order to reduce labour costs, but also rapid polishing usually meant that less of the precious silver deposit was lost in the polishing process. The silver plater early became conscious of the fact that silver could be deposited both as a "hard" plate, and a more desirable "soft" plating. Subsequent research confirmed that there were definite variations in the physical properties of deposited silver with the conditions of deposition, but what the silver polisher considered to be hard was actually softer than the desired type of deposit. It was the closely grained ("hard") silver deposit which produced a more rapid lustre when pressed against the polishing mop.

The use of carbon disulphide is employed to this day, old silver-plating works possessing their own time-honoured methods of adding this brightening agent. For example, in some establishments it is usual to add the disulphide to some of the solution placed in a bottle, and to keep this locked in a dark room to "age," the addition being made periodically, almost as a solemn rite.

In recent years considerable light has been shed on the mechanism of brightening by carbon disulphide addition, while also other addition agents have been put forward to brighten the deposit. Addition of carbon disulphide was suggested as early as 1847 by Lyons and Milward.(1)

Many of the newer addition agents contain sulphur in one form or another; thus, for example, a recent patent (2) proposes the addition of thiourea. The addition of sodium thiosulphate was put forward in a paper published in the *Transactions of the Electro-*

chemical Society in 1931.(3) Other substances are groups of aliphatic acids and compounds such as Turkey red oil,(4) cyanates,(5) and even nitrates.(6)

Taking the standard solution of silver, containing the following constituents :—

Silver	20 grms.
KCN (Free)	36 ,,
K_2CO_3	22 ,,
Water	1 litre

a smooth dull deposit is obtained at 6 amps./sq. ft. If thiourea is now added no effect is obtained up to 0·1 grm./litre, but as the concentration is increased thereafter the deposit brightens, and at 35 to 40 grms./litre the brightness is said to be greater than that obtainable by the use of carbon disulphide, although the deposit may possess a slight haze (which, however, can be readily cleared).

The current density range for obtaining bright deposits is low and of the order of 5 to 8 amps./sq. ft. The free cyanide content must be between 20 and 50 grms./litre to achieve maximum brightness. The solution assumes a red colour, a black precipitate (not sulphide) being at times formed. The *p*H appears to have some effect, since by acid addition, for example boric or acetic acids, the brightness increases still further.

While urea does increase brightness it is not as effective as thiourea. With regard to thiocyanates, the potassium salt appears to be reasonably satisfactory as an addition agent; the ammonium salt is not very satisfactory, as the free ammonia which forms on standing is undesirable.

Among other organic substances which have been found to act as brighteners, is thiosemicarbazide. On the other hand, the following substances do not produce a brightening action—cyanamide, guanidine, ammonium thiocyanate, cyanuric acid, and methylamine.

In a recent patent (7) the production of bright deposits from silver cyanide solutions is considered, using the following groups of addition agents :—

(1) Organic sulphides of the carbon disulphide and mercaptan groups.

(2) Alkali salt of a soap forming acid, or of a sulphonic acid derived from a soap forming acid.

The grain-size reduction which is thereby effected may be further assisted by addition of a glycerol or glycol.

Examples of bright plating solutions are the following:—

Example No. 1

Silver	2·0 ozs./gallon.
Free cyanide	8·0 ,,
Turkey Red oil	0·75 ,,
Sulphide brightening solution	0·75 ,,

Example No. 2

Silver	3·0 ozs./gallon.
Free cyanide	6·0 ,,
Castile soap	3·0 ,,
Sulphide brightening solution	0·75 ,,

The sulphide brightening solution is prepared by saturating a portion of the plating solution with carbon disulphide. Current densities up to 8 amps./sq. ft. may be employed.

A novel addition in the form of a selenide is proposed by R. Weiner.(8) At a fairly high current density, *i.e.*, 20 to 30 amps./sq. ft., bright deposits are obtained provided rapid movement of the cathode liquor or the cathode is maintained. The hardness of the deposit is considerably higher than that obtained from the ordinary silver electrolyte owing to its structure, and hardness has therefore to be reduced by heat treatment. The Weiner process is patented and used by the Deutsche Gold und Silber Anstalt.

SOURCE OF BRIGHTENING IN CARBON DISULPHIDE ELECTROLYTES

In a preliminary study by B. Egeberg and N. E. Promisel, made in 1938(9) and based on the assumption that carbon disulphide is not the real brightening agent, an empirical formula was arrived at which is indicative of the real source of brightening of the deposit. Egeberg and Promisel were led to conduct this study owing to the impossibility of controlling the carbon disulphide in the solution. Being present in very small quantity, it is difficult to control by analysis, and therefore very largely the efficiency of the process is determined by the skill and experience of the operator. The authors determined the brightening effect of a number of organic compounds, with the following main results.

A number of organic compounds were employed of a type which, it was thought, might be formed in the bath as a result of interaction between the constituents. Examples of such compounds are urea, thiourea, cyanamide, etc. As a result, it was possible to divide the compounds examined into two groups, (*a*) those which resulted in a brightening action, and (*b*) those which did not. Compounds in these respective categories are listed as follows:

(A) Substances which actively brighten.

Thiourea 

$SC\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$

Urea 

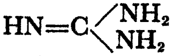
$OC\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$

Potassium Thiocyanate
$N{\equiv}C\text{-}S\text{-}K$

Thiosemicarbazide
$H_2N{-}CS.NH.NH_2$

(B) Substances which do not actively brighten.

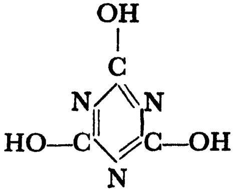
Cyanamide $N{\equiv}C{-}NH_2$

Guanidine 

$HN{=}C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$

Ammonium Thiocyanate
$N{\equiv}C{-}S{-}NH_4$

Cyanuric Acid



Methylamine
$H_2N{-}CH_3$

From this it is observed:—

(1) That all brightening compounds possess at least one nitrogen atom and a sulphur or oxygen atom attached to a carbon atom.

(2) No compounds in class "B" possess a sulphur atom attached to a carbon atom, except only ammonium thiocyanate. The latter compound eventually produces ammonia in solution, which was found in the experimental work to be detrimental to brightening, and therefore the non-brightening properties of this compound are ascribed to ammonia formation.

(3) In the "A" class, where the sulphur atom is interchangeable with the oxygen atom, it is the former which is the more effective in its brightening action.

As a result, the first tentative conclusion is that a class of organic compounds having the following nucleus (or a closely analogous arrangement of these elements) favours brightening:—

$$=N{-}CS{-} \quad = N{-}CS \text{ or } = N{-}CO{-}$$

Since it was found that ammonia-forming or any general alkali-forming compounds are undesirable, and that the presence of two nitrogen atoms attached to the carbon atom is preferable, while, further, the presence of more than one sulphur atom might be desirable, the authors postulated the following general formula as a basic brightener :—

$$\mathrm{CSx\ (NA)\ (NB)}$$

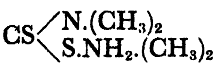
(Oxygen may replace sulphur in this formula.)

" A " and " B " must not tend to increase the alkalinity of the solution. On this basis, the following compounds were considered :

(1)

$$\mathrm{CS}\begin{matrix}\diagup \mathrm{NH.CH_3} \\ \diagdown \mathrm{S.NH_3.CH_3}\end{matrix}$$

(2)



$$\mathrm{CS}\begin{matrix}\diagup \mathrm{N.(CH_3)_2} \\ \diagdown \mathrm{S.NH_2.(CH_3)_2}\end{matrix}$$

(3)

$$\mathrm{CS}\begin{matrix}\diagup \mathrm{NH.C_2H_5} \\ \diagdown \mathrm{S.NH_3.C_2H_5}\end{matrix}$$

these being derivatives of an aliphatic primary amine, secondary amine and homologous primary amine respectively. (The *aromatic* compounds analogous to these are not soluble in the silver cyanide solution.)

The interesting fact emerged that all of these compounds used in extremely small amounts (of the order of 0·1 c.c. per litre) were found to possess marked brightening action on the silver, and under correct conditions of current density, temperature and solution composition, mirror bright deposits were achieved.

Of the compounds examined, the methylamine derivatives were found to be the most effective, particularly the primary methyl compound.

The authors concluded that the generic formula indicates the type of compound which is what carbon disulphide is actually converted to, before it can exert its major brightening action.

BRIGHT DEPOSITS FROM ACID SOLUTIONS

While the cyanide solution is universally employed industrially, a fair amount of work has been carried out in the laboratory to examine what possibilities exist to produce bright deposits from the acid solution, of which the most common is that based on silver nitrate. So far as the author is aware, no successful commercial process has yet developed as a result of this work.

Some of the early work in this field was carried out by the present author some considerable time ago.(¹⁰) In this work the effect of a number of colloids when added to a silver nitrate solution was determined. The actual aim of the research was to see if it was possible to obtain a parallelism between the effectiveness of a colloid in reducing grain-size and the "gold number" of that colloid. Since silver solutions were used, however, an equivalent "silver number" was obtained for each colloid employed in the work, and a rough parallelism was in fact discovered.

However, for the present purpose it will be sufficient to indicate that it was found possible to reduce the grain-size of the silver deposit from its nitrate electrolyte very considerably. The grain-size was obtained by actually counting the number of crystals per unit area, and the table below indicates the results obtained with some of the colloids. In no case, however, was a deposit obtained which approached the brightness of silver obtainable from a cyanide electrolyte to which a brightener has been added.

TABLE VII

Electrolyte.	Appearance of deposit.	Average No. of Crystals per cm^2.
$AgNO_3$ alone	Coarsely crystalline; big variation in sizes of crystals	71×10^4
$AgNO_3 + 0{\cdot}02\,\%$ gum tragacanth.	Close-grained deposit	523×10^4
„ gum acacia.	Very small crystals	356×10^4
„ gum arabic	Close-grained deposit: white	380×10^4
„ gelatin	Small crystals; white deposit	335×10^4
„ starch	Bright deposit; varying crystal size	218×10^4
„ dextrin	Dark deposit; close-grained.	554×10^4
„ glucose	Large flat crystals; white	97×10^4
„ β-naphthol	Voluminous, non-adherent crystals	28×10^4
„ dextrose	Voluminous, non-adherent crystals	31×10^4

Some ten years later, R. Taft and L. H. Horsley (¹¹) extended this work considerably by employing a large number of addition agents of varying types. They employed about 140 organic materials and about 30 inorganic compounds. The results obtained were correspondingly diverse. The deposits were classified under five headings, namely.

(*a*) Fine;
(*b*) Intermediate,
(*c*) Control;
(*d*) Abnormal;
(*e*) Striated;

the control being equal to a deposit obtained from a bath containing no addition agent

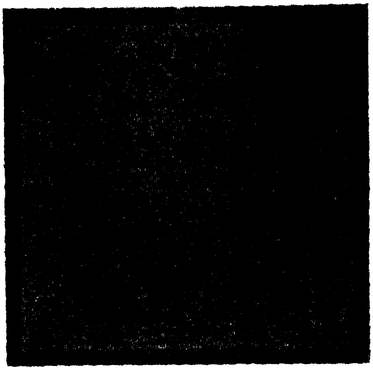


Fig 40—Control deposit ×2

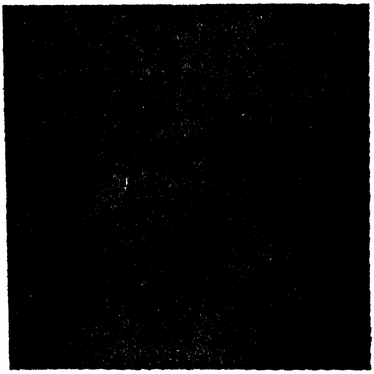


Fig 41—Addition agent—benzillic acid ×2

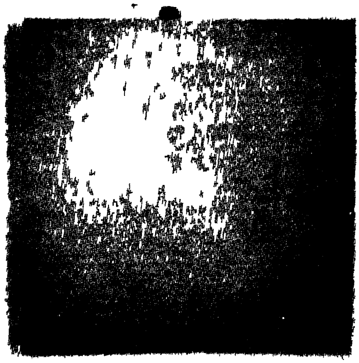


Fig 42—Addition agent—malic acid ×2.

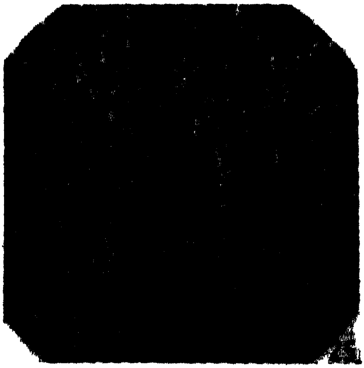


Fig. 43—Addition agent—tartaric acid ×100.

Effect of addition agents in depositing silver from acid electrolytes (due to R, Taft, L H. Horsley)

Of 169 deposits, the following results were obtained:

Fine	26
Intermediate	15
Control	67
Abnormal	14
Striated	43
Unclassified	4
Total	169

This indicates the comparatively few addition agents which resulted in any refinement of the grain-size.

Of the "fine" deposits, the classes of compound which were effective were as follows:—

Aliphatic acids (or salts)	15
Cyclic acids	4
Inorganic salts	2
Dyes	2
Miscellaneous	3

The best deposits in the "fine" group were obtained by the use of the following substances—isovaleric acid, lactic acid, methylene blue, succinic acid, sodium hydrogen arsenite, benzilic acid, sodium acetate and ferrous sulphate. Thus, 19 out of the 26 substances producing the fine deposits were organic acids or their salts.

In general, it was found that colloids of high molecular weight (above 250) produced abnormal or striated deposits. On the other hand, smooth, fine crystalline deposits resulted when certain higher aliphatic and cyclic acids were added. The lower fatty acids, *i.e.*, acetic and proprionic, were found to be ineffective.

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(9) B. Egeberg and N. E. Promisel, "Brighteners in Silver Plating Solutions," *Trans. Electrochem. Soc.*, 1938, Preprint 74-13.
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CHAPTER IX.

Electrolytic Polishing of Copper and Silver

REFERENCE has already been made in Chapter I of this book to one or two solutions which have been employed in the electrolytic polishing of copper (and also brass) for metallographic purposes in particular. Jacquet obtained some excellent results employing pyrophosphoric acid as an electrolyte.(1) He employed a 53 per cent. solution, a current density of 8 to 10 amps./sq. dcm., and a voltage of 1·6 to 2. The temperature of the solution was 15°C. to 22°C., and the time required to obtain a polish was 10 to 15 mins., the initial polish on the surface having been produced by 00000 paper.

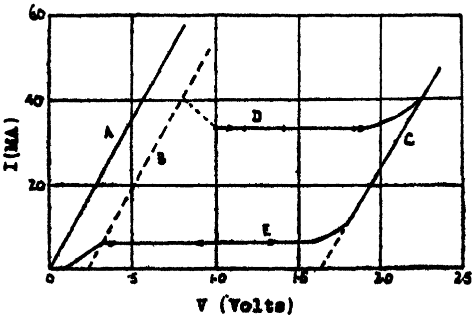

Fig. 44.—Voltage-current cuves obtained for the the polishing of copper (room temp.)
(W. C. Elmore, "Journ. of Applied Physics," 724, 10, 1939.)

Lowery, Wilkerson and Smare (2) report good results using orthophosphoric acid (specific gravity 1·3 to 1·5) at a much lower current density, *i.e.*, approximately 0·7 amps./sq. dcm., and a voltage of 2, with the solution at room temperature. Using material which had been polished to 0000 paper, the time of producing the necessary effect was something in excess of 5 mins.

W. C. Elmore (3) in the course of an investigation of electrolytic polishing on copper and iron, made use of the Jacquet electrolyte and found this entirely satisfactory.

L. von Hámos, a Swedish investigator who published an interesting paper in 1942,([4]) made use of an orthophosphoric acid solution, the concentration of which was very similar to that of Lowery, Wilkerson and Smare. The specific gravity was 1·25. The conditions, however, were very different in that a current density of the order of 25 to 35 amps./sq. dcm. was employed at a comparatively low bath temperature (12°C.). Furthermore, the electrolyte was stirred by means of a paddle, the rate of rotation being some 60 revs. per min. The state of the surface initially was produced by emery No. 00.

Brass specimens were similarly treated with good results.

Von Hámos has some interesting things to say respecting the composition of the specimen being polished, the degree of surface preparation necessary, etc. It is proposed to deal with these at greater length later.

However, with regard to the degree of surface preparation, it is interesting to give Von Hamos' views at this juncture, since his opinion is that, for given electrolytic conditions, every degree of surface grinding requires its particular optimum current density and time. If, for example, a relatively coarsely ground surface has to be electrolytically polished, then usually it is necessary to employ an electrolyte of high conductivity in order to dissolve away the surface of the specimen as rapidly as possible. A solution of lower conductivity will usually work more slowly and will therefore not level out surface irregularities of considerable coarseness. An interesting observation made by this author is that it is possible, on the other hand, for a very smooth initial surface to be actually detrimental to electrolytic polishing. This is said to be due to the fact that a comparatively smooth surface has not the capacity to supply in a short time the material necessary for the skin to be formed.

G. J. Foss, Jr. and Larry Shiller ([5]) state that they have found an electrolyte consisting of 25 to 55 per cent. of commercial orthophosphoric acid (85 per cent. H_3PO_4) satisfactory. Whereas some investigators have suggested that best results are obtained if the anode be held horizontally, these authors found that in this solution position of the cathode did not particularly influence the results. A small anode/cathode distance is recommended, *i.e.*, from ½ in. to 2 in. between the electrodes. The cathode should preferably be considerably greater in surface area than the anode; the cathode material can be brass or copper.

The current voltage curve for this electrolyte is typical and is shown in Fig. 45. The current rises with the application of increased voltage, until the point C, metal being removed from the anode without any noticeable brightening at this juncture. From C to C′ there is then a perceptible drop in current and anodic brightening commences, this continuing from C′ to D, the current density remaining fairly steady despite changes in voltage. At D the current increases suddenly and gas is evolved. The gas bubbles adhere to the anode, these localities then ceasing to be further polished and resulting in local marks. If, however, the current density be raised considerably, the gas evolution is so rapid that the bubbles do not adhere and a polished surface free from local blemishes is produced.

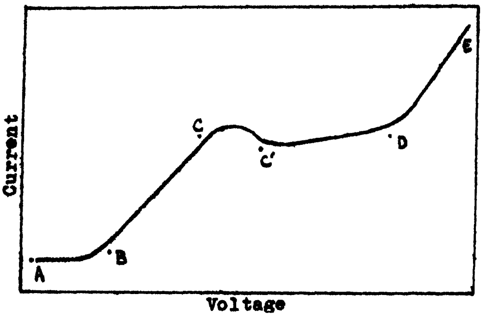

Fig. 45.—Current-voltage curve for electrolytic polishing of copper or brass in orthophosphoric acid solutions. (Due to G. J. Foss and L. Shiller.)

Foss and Shiller found that better results were obtained when the electrolyte was aged, there being some difficulty in holding the voltage at a desired value when it was freshly made up. When, however, the electrolyte contained a certain amount of copper in solution, it appeared to stabilise and the polishing improved. As time goes on and the copper content increases, the current-voltage figures also alter, the whole of the curve shown in Fig. 41 tending to be displaced towards the left; thus the necessary voltage decreases as also does the current density.

The authors emphasise the importance of determining the current voltage curve for any particular solution concentration and any particular set-up of the electrodes. If agitation be employed, the voltage tends to drop and to vary considerably. Filtration should be employed in order to remove metal particles which accumulate.

When the specimen has been polished, it should be removed promptly just before the current is cut out, as otherwise a back e.m.f. may be set up causing copper to deposit on the surface. Should a white film remain after washing and drying, it can be removed by immersing in a dilute solution of orthophosphoric acid.

G. C. Williams and G. Rieger (6) have reported satisfactory results from the use of the following solution:—

Ammonium acetate (0·10M)	10 ml.
Ammonium hydroxide (0·14M)	30 ml.
Sodium thiosulphate (0·50M)	30 ml.
Distilled water	30 ml.

A current density of the order of 2 amps./sq. ft., a stainless steel cathode (optimum size 15 sq. in. for an anode area of 1·5 sq. in.), and an anode/cathode distance of about ¾ in. are the conditions employed for a period of about 10 secs. This method is applied to copper and brass specimens in which only one phase (the alpha phase) is present. Should there be more than one phase, it is only the alpha phase which is polished, the beta phase being attacked.

ELECTROLYTIC POLISHING OF SILVER

The electrolytic polishing of silver has received some attention in recent years. One of the most interesting studies on this subject was made in 1942 by L. I. Gilbertson and O. M. Fortner.7) They employed a bath commonly used in silver plating, and containing the essential constituents—silver cyanide, potassium cyanide and potassium carbonate and were successful in obtaining electrolytically polished silver, the reflectivity of which was easily as high as that produced by mechanical polishing.

Hedges (8) had already observed the periodic formation and dissolution of an anode film with the passage of time under certain electrolytic conditions. At the critical current density, the surface of the anode became bright, and with continued formation and solution of the film the surface became smooth.

Gilbertson and Fortner determined the effect on the current density *versus* anode potential relationship of the independent variables; bath composition, temperature and stirring rate.

EFFECT OF FREE CYANIDE

Increase in concentration of free cyanide was found to increase the critical current density at which the electro-polishing took place.

(See Fig. 46.) On the other hand, the effect of adding salts other than cyanides to the bath was to increase the conductivity of the bath and to *lower* the critical current density.

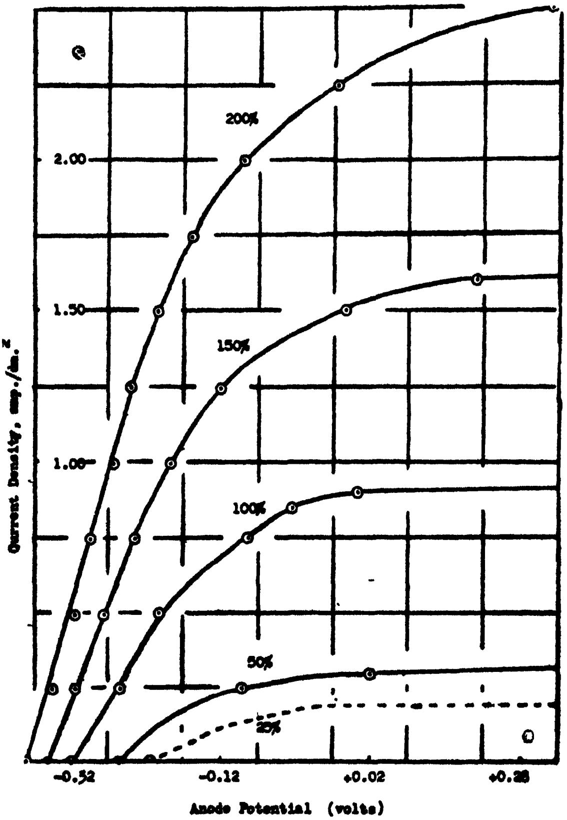

Fig. 46.—Effect of free cyanide concentration on current-density anode potential relationship. (Due to Gilbertson and Fortner.)

Concentrations normally employed in silver plating baths, *i.e.*, say, 100 per cent. free cyanide and about 40 grms./litre of potassium carbonate, were found to be satisfactory in the production of the anodic polish.

EFFECT OF TEMPERATURE

Rise in temperature was found to increase the critical current density. There is therefore no advantage in using temperatures above normal, and 25°C. was taken to be a normal temperature to study further effects.

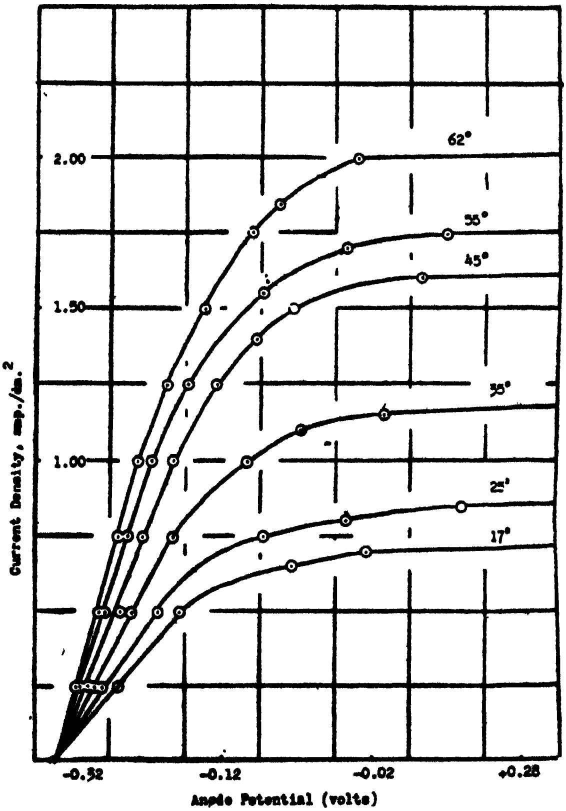

Fig. 47.—Effect of temperature on current density-anode potential relationship. (Due to Gilbertson and Fortner.)

EFFECT OF STIRRING

Stirring, or rather the rate at which stirring took place, was found to have a very pronounced effect. Increasing the rate of stirring increased the critical current density, and therefore high stirring rates were found to be undesirable. Since, however, layer formation occurred in still solutions, a low stirring rate was nevertheless found to be necessary to obviate this tendency.

The conclusions arrived at by the authors were as follows:

Confirmation of the fact that the electrolytic polishing process consists in the progressive reduction of projections on the surface of the anode was strikingly shown in the course of this work, the various stages having been photographed to illustrate the course of the action. Figs. 49, 50 and 51 respectively illustrated the dissolution process which proceeds at the anode as the electrolysis continues; while the effect is again shown in Fig. 52, which illustrates an unpolished electro-deposited silver surface after electrolytic polishing treatment. A graphic representation of the process is shown in Fig. 53.

The authors' theory of the mechanism of formation and dissolution of the anode film is very similar to that suggested by Hedges.(8) It is thought that at low current densities the anode dissolves in the usual manner, forming an argentocyanide anion and leaving the anode surface crystalline. On raising the current density, the rapid formation of silver ions at the anode surface, accompanied by a corresponding diminution in cyanide ions, results in precipitation of silver cyanide which appears, at first, as a grey film on the anode. The film of silver cyanide accumulates first in the depressions and then over the whole surface, and since it is a poorer conductor than the metal, dissolution of the projections takes place during this phase of the cycle. Meantime, the anode potential rises rapidly

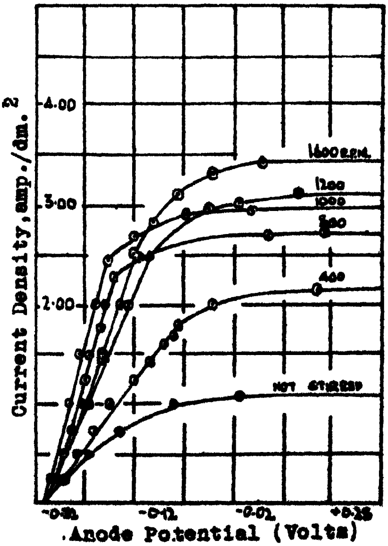

Fig. 48.—Effect of rate of stirring on current density-anode potential relationship. (Due to Gilbertson and Fortner.)

with decrease in current density and silver oxide is formed as a result of the hydrolysis of the silver cyanide, due to increased hydroxyl ion concentration at the anode. The oxide film is unstable, and as a result of its metastability, forms silver cyanide.

Fig. 49.—Electrodeposited silver
Unpolished ×200

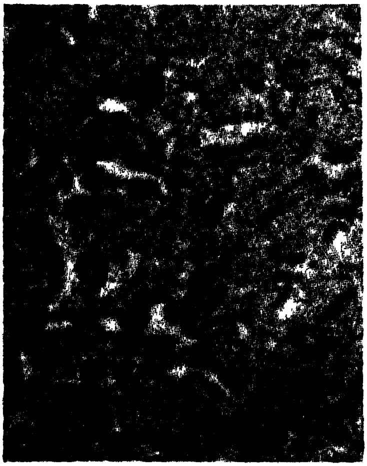

Fig. 50.—Electrodeposited silver
Electropolished for 3 minutes ×200

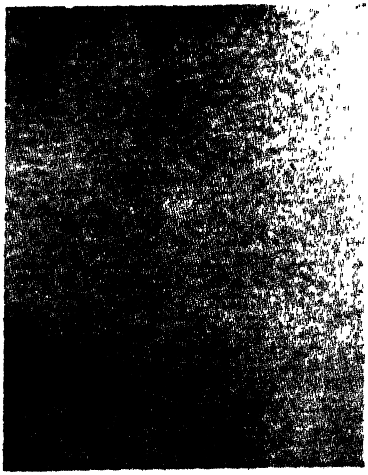

Fig. 51.—Electrodeposited silver.
Electropolished for 9 minutes ×200.

The metal surface is then in contact with the solution, and with the return of the original current density—anode potential relation, the cycle repeats itself. The factors which control the rate at which the cycle repeats, are—rise in current density (*decreasing* the frequency), and rise in temperature and concentration (*increasing* the

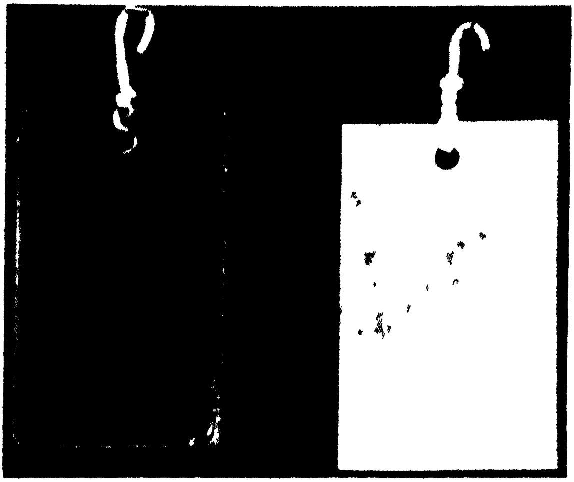

Fig. 52.—Left: Electropolished, electrodeposited silver
Right: Unpolished electrodeposited silver

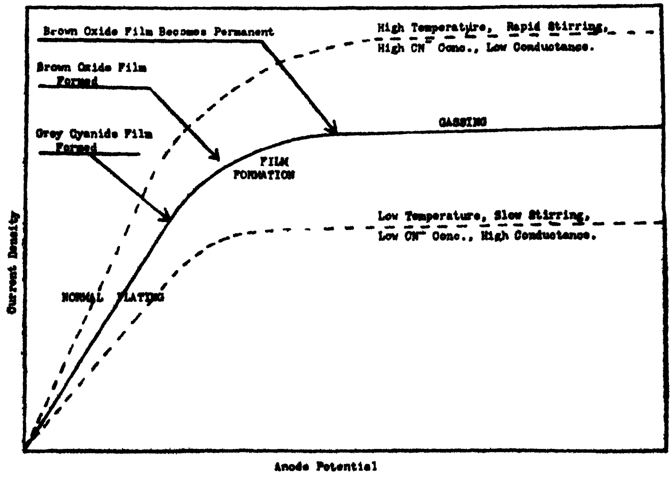

Fig. 53.—The process of electropolishing
(Due to Gilbertson and Fortner.)

frequency). Additionally, however, the authors concluded that the rate of stirring is a very critical factor, this being due to the fact that it helps the dissolution of the film, in bringing up fresh cyanide to the anode.

It is apparent that whatever development may subsequently arise in the field of electrolytic polishing of silver, its success will depend very largely on careful control of the major factors affecting the production and dissolution of the anode film.

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CHAPTER X.

Deposition of the Precious Metals Platinum and Palladium

IT is opportune to come now to a consideration of the possibilities of producing bright deposits in that group of metals which is commonly termed the platinum or precious metals group. In this group we have, in addition to platinum, the following metals—palladium, rhodium, iridium, ruthenium, and osmium.

Platinum, which gives its name to this group, was discovered some 200 years ago, and although its use in the electrodeposition field is not great, it is interesting to note that as far back as 1887 there existed a company called The Bright Platinum Plating Company, which patented various solutions for depositing this metal. Possibly this constitutes one of the earliest applications of bright metal deposition, excepting only silver, which was probably the first of all the metals to be deposited in a bright form. The Bright Platinum Plating Company claimed, even then, that the baths produced so bright a deposit that further polishing was not necessary—a claim which has a familiar ring to-day in connection with various metal deposits which have already been considered in previous chapters.

The prime attraction of the platinum group of metals lies in their corrosion resistance, especially under atmospheric conditions. Production of a bright deposit by electrolytic means therefore results in a permanent degree of polish on the metal surface. The disadvantage, on the other hand, is the obvious one of cost, since all metals in this group are necessarily expensive. None the less, it has been found that surprisingly thin deposits are sufficient to provide valuable surface characteristics to a basis metal, and applications are therefore not lacking for some of these processes. Again, it is possible, as with chrome, to reinforce the precious metal deposit by a substantial heavy undercoating of another deposit, such as nickel or copper, and so overcome porosity to a considerable extent. It may be objected that chromium is considerably cheaper than any of the precious metals and is also tarnish-resisting to the atmosphere. While this is true in general, there are, nevertheless, many applications where a deposit which is more attractive in colour than chromium is required, or where other properties, such as high reflectivity, make one of the precious metals the better choice.

PHYSICAL PROPERTIES

The following tables (¹) summarise the important physical characteristics of those metals in the platinum group in which considerable interest has been shown in recent years—namely, platinum, palladium, and rhodium.

TABLE VIII

PHYSICAL PROPERTIES

———	Platinum	Palladium	Rhodium
Atomic weight	195·2	106·7	102·9
Specific gravity . . .	21·44	12·16	12·41
Melting Point	1773°C.	1553°C.	1966°C.
Temperature coefficient of linear expansion, per ° C. ...	$8{\cdot}9\times10^{-6}$	$11{\cdot}8\times10^{-6}$	$8{\cdot}5\times10^{-6}$
Reflectivity (visible spectrum)	65	65	78
Specific resistance, annealed; 20°C.; ohm$-$cm.$^3\times10^{-6}$ ...	9·97	10·78	4·3

TABLE IX

ELECTRODEPOSITION DATA

	Platinum	Palladium	Rhodium
Theoretical rate of electro deposition for 100 per cent. current efficiency. Grms. per amp. hr.	3·64 (valency =2) 1·82 (valency =4)	1·99 (valency =2)	1·28 (valency =3)
Weight of deposit of 0·00001 in. thickness mgrm. per sq. in.	3·51	1·99	2·03
Normal electrode potential at 20°C., volts (²)	0·86 to 0·93	0·71 to 0·73	0·67 to 0·68

TABLE X

HARDNESS DATA.

——	Annealed B.H.N.	Hard Rolled B.H.N.	Cast B.H.N.	Electrodeposited
Rhodium	101 (3)	—	101 (3)	594-641 D.P.H.N.
Platinum	47	97	50	606-642 D.P.H.N.
Palladium	49	109	52	387-435 D.P.H.N. Hard 190-196 D.P.H.N. Soft
Nickel	70-90*	90-300*	70-90*	155-420 B.H.N.
Chromium	—	—	91	500-900 B.H.N.
Silver	25	68	30	61-79 B.H.N. Matt 130 B.H.N. Bright

* Standard 99 per cent. commercially pure "malleable" nickel.

Certain points of interest are immediately apparent in examining these tables. Firstly, it is obvious that platinum is by far the densest metal, and therefore approximately twice as much platinum must be deposited as either of the other metals to achieve approximately the same thickness (this, of course, assumes that the current density employed is the same throughout).

The second point of interest is the remarkably high melting point of all the metals, particularly that of rhodium.

Thirdly, the high reflectivity of rhodium compared with the other two metals may be noticed, and as will later be indicated, this property, related as it is to the comparative reflectivity of silver and its tarnishing characteristics, makes rhodium a highly important surfacing material for reflectors.

Fourthly, it is interesting to note the fact that all the platinum metals can be deposited in a state of considerable hardness. In this connection, a useful comparison is drawn in Table X with the common electrodeposits, nickel, chromium, and silver, from which it is apparent that only deposited chromium exceeds rhodium and platinum in hardness, although nickel can be deposited in its higher ranges of hardness in a form comparable with, at any rate, palladium.

PLATINUM PLATING

The deposition of this metal actually goes back over a century, since the first mention of a process of this kind was by Böttger in 1840. At the time, he was endeavouring to produce a metal coating on copper plates used in printing practice. Using as an electrolyte platinum chloride and sodium chloride in approximately equal proportions, he claimed to produce a white platinum deposit on copper, which was later considerably improved by changing the electrolyte to ammoniated ammonium chlorplatinate (used hot), the deposit produced being then resistant to nitric acid.

There was evidently considerable interest in platinum deposition processes at about this time, since some three or four processes were suggested during the 1840's. However, it was not until 1855 that a really effective electrolyte was produced. This was a bath detailed by Roseleur and Lannaux. The instructions for its preparation were quite clear.

" One takes 750 grams sodium phosphate and 400 grams sodium pyrophosphate and dissolves in 15 litres of water, and filters. One also takes 15 grams of platinum chloride, as free as possible from acid, dissolves it in 200 grams distilled water, and precipitates the platinum as double salt by adding 160 grams ammonium phosphate. The precipitate, together with the supernatant liquid, is mixed with the first-mentioned solution and boiled for four hours. Ammonia escapes, and the bath, previously alkaline, becomes strongly acid; the liquid loses its yellow colour, and can now be used successfully for platinum plating, also for thick deposits."

Meantime, some ten years later, Böttger claimed to have produced a highly brilliant deposit from a bath containing ammonium chlorplatinate in a concentrated solution of sodium citrate, and in 1887 the Bright Platinum Plating Company patented the Roseleur and Lannaux solutions with the addition of borax and common salt.

Before the turn of the century it began to be realised that one of the greatest difficulties in the uniform production of the platinum deposits was the fact that in the solutions so far employed, inert salts were gradually built up and accumulated, and in time affected the quality of the deposit. Abandoning the use of chlorides, Wahl developed an electrolyte containing essentially platinic hydrate and oxalic acid, from which good platinum deposits were produced.

Various other baths were proposed, but none showed any considerable improvement on the Roseleur process until the work of Keitel and Zschiegner.(4)

It was not until round about 1930 that two distinct types of baths were independently developed, showing a definite improvement on the old process. The first, due to Keitel and Zschiegner, is based on the preparation of dinitro-diammino platinum. The second, due to Powell and Scott,(5) is based on the use of an alkali platinate electrolyte.

The preparation of these platinum compounds is not simple, and details are therefore appended of the manner in which they are produced.

(1) KEITEL AND ZSCHIEGNER PROCESS

The dinitro-diammino platinum is prepared from a solution of platinum chloride; to this a sodium nitrite solution is added, this resulting in a colour change from orange to a lightish yellow, while the nitrous gases are given off. The resultant solution is heated until the reaction is completed, and then a slight excess of ammonia is added when the electrolyte has cooled. The precipitate formed is dinitro-diammino platinum, and requires filtration and washing free from alkali before use. A solution may then be made up as follows:—

Platinum diammino nitrite $[Pt(NH_3)_2 (NO_2)_2]$	2·2 oz.
Ammonium nitrate	13·4 oz.
Sodium nitrite	1·3 oz.
Ammonia (28 per cent. solution)	6·7 oz.
Water	1 gallon

The platinum diammino nitrite is rendered more soluble by dissolving it separately in a heated 5 per cent. ammonia solution. The bath is operated at high temperature—*i.e.,* about 95°C., and therefore requires replenishment of the ammonia at fairly frequent intervals. A current density of about 4 amps. per square foot is employed.

The cathode efficiency of this bath is not high, but the throwing power is reasonably satisfactory, and a good deposit is obtainable within 5 to 10 minutes of deposition. The solution is replenished periodically by the addition of further platinum diammino nitrite (dissolved in ammonia).

According to K. Schumpelt (6) the ammonium nitrate reacts with the sodium nitrite according to the following equations:—

$$NH_4NO_3 + NaNO_2 \rightleftarrows NH_4NO_2 + NaNO_3$$
$$NH_4NO_2 \rightleftarrows N_2 + 2H_2O$$

and no objectionable salts are built up in the electrolyte. The nitrite ion concentration has a tendency to rise, possibly as a result of the cathodic reduction of the nitrate ion. The increase in nitrite ion content throws back the dissociation of the platinum diammino nitrite, thus reducing the platinum metal ion content which affects the cathode efficiency deleteriously. This can be countered by the addition of a certain amount of ammonium nitrate and heating the bath to boiling, which results in the decomposition of the excess nitrite.

The brightest deposits are obtained when the *p*H is below 7, but in any case it must not fall below about 6·5, and a *p*H of about 6·8 is advisable for everyday work.

(2) POWELL AND SCOTT PROCESS

In this case the solution is made up as follows:—

"100 ounces of sodium chloroplatinate ($Na_2PtCl_6 6H_2O$) are dissolved in six gallons of hot water and 100 ounces of sodium hydroxide in solid form are then added to the hot solution. The liquid boils vigorously, so that cold water must be added as required to keep the boiling under control. When all the sodium hydroxide has been added, the solution is diluted to 12 gallons with hot water, and boiling is continued for from three to four hours until the colour of the liquid changes from orange to pale yellow; when the liquid has cooled slightly, a solution of 16 ounces of oxalic acid is added to form 17 ounces of sodium oxalate in the mixture, and this is followed by 37 ounces of sulphuric acid diluted with water. The platinum solution will now contain 17 ounces of free sodium hydroxide, and after dilution to 24 gallons, it contains approximately 1 per cent. of platinum and 0·5 per cent. of free sodium hydroxide. The sodium chloride, formed by the reaction of the sodium hydroxide with the sodium chloroplatinate, and the sodium sulphate, formed by the subsequent partial neutralisation with sulphuric acid, act as conducting salts and increase the conductivity and throwing power of the plating bath.

"If an excess sulphuric acid be added to the solution resulting from the reaction of the sodium hydroxide with the sodium chloroplatinate, a precipitate of hydrated platinic oxide (PtO_2, $4H_2O$) is obtained; this precipitate may be washed free from soluble salts and dissolved in sodium hydroxide solution to yield an alkali metal platinate solution from which a plating bath may be prepared by adding sufficient sodium hydroxide to give a free alkalinity of less than 2·5 per cent., and preferably of from 0·2 to 1·0 per cent., the requisite quantity of sodium oxalate, for example, 0·5 per cent. and sufficient sodium sulphate, for example, 3 per cent., to give a good throwing power."

The conditions of operation are as follows:

Current density up to 20 amps./sq. ft.
Temperature, 65 to 85°C.

The current efficiency of this bath is claimed to be 100 per cent., and bright and adherent deposits of platinum are obtained without difficulty. This is confirmed by R. H. Atkinson, who, however, points out that the electrolytes are not perfectly stable, since if kept for any lengthy period they result in considerable precipitation, the supernatant liquor then producing only poor deposits.

E. C. Davies and A. R. Powell have given some very interesting data concerning their bath in one of their publications.(7)

In this account of their work, the authors state that they concentrated their efforts on the production of an alkali platinate electrolyte, and endeavoured to obtain a solution which employed caustic soda rather than caustic potash as the alkali base; this because caustic potash first produced a precipitate of potassium chloroplatinate, which is rather difficult to decompose when further alkali is added.

In their own words: " When chloroplatinic acid is boiled with caustic soda, the yellow colour of the solution gradually disappears and, if sufficient water is boiled away, a heavy, almost white, crystalline precipitate of sodium hexahydroxyplatinate, $Na_2Pt(OH)_6$, $3H_2O$, separates. Although these crystals will redissolve slowly when hot water is added, it is better to avoid their formation during the boiling process by adding more water from time to time. In any case, either solution will give a good plate during the early stages of use as a plating bath. We soon found, however, that continuous bright plating could be obtained only by a strict control of the amount of free alkali hydroxide present. Wahl recommended about 4 per cent. of free hydroxide, but our experiments indicated that about one-tenth of this amount gave far more satisfactory results. Although the presence of chloride in the bath did not prevent bright plating, we discovered that a chloride-free bath operated much more satisfactorily. Further work showed that the presence of silicate in the solution was objectionable, since small amounts tended to produce rough and patchy deposits, and large amounts very matt deposits. Addition of sodium oxalate to the bath was found to improve the stability, and of sodium sulphate to increase the conductivity and throwing power."

They then turned their efforts in the direction of producing a salt which would readily dissolve in water, this salt being sodium hexahydroxyplatinate, $Na_2Pt(OH)_6, .3H_2O$. The solution was then prepared as follows: –

150 oz.* of sodium chloroplatinate ($Na_2PtCl_6, 6H_2O$), are dissolved in 2 gals. of hot water and the solution is added to 3 gals. of hot water containing 15 oz. of sodium hydroxide. 135 oz. of sodium hydroxide in solid form are then added to the hot solution. The solution boils vigorously, so that cold water must be added as required to keep the boiling under control. When all the sodium hydroxide has dissolved, the solution is diluted to 15 gals. with hot water and boiling is continued for 3 to 4 hours, until the colour of the liquid changes from orange to pale yellow. The solution is then cooled to 20°C., and 10 to 15 gals. of commercial ethyl alcohol are added while stirring constantly, whereby a finely crystalline precipitate of sodium hexahydroxyplatinate is obtained. After the precipitate has settled, the clear liquor is siphoned off and the crystals are collected on a vacuum filter, washed with a mixture of equal volumes of alcohol and water, then with alcohol alone, and finally with acetone. The crystals are dried in a current of air at a temperature preferably not exceeding 40°C. until a fine crystalline powder is obtained. Overheating must be avoided as the organic liquid reduces the salt to platinum black at high temperatures Under the conditions specified about 88 oz. of the salt are obtained, containing 54·4 per cent. of platinum and representing about 94 per cent. of the platinum used in the manufacture.

The solution is then made up from the following formula:—

Sodium hexahydroxyplatinate ...	2·7	ounces
Caustic soda	0·75	„
Sodium oxalate	0·75	„

---

* 1 oz. Av. = 28·4 g. 1 gallon = 4·54 litres.

Anhydrous sodium sulphate	4·5	,,
Water	1	gallon

Distilled water should preferably be used, and either a rubber-lined or nickel tank employed as a container.

CONDITIONS OF OPERATION

Current density.—This may vary from 3 to 15 amps. per sq. ft., and a safe figure is about 8 amps., as the risk of "burning" the work is then reduced.

The current efficiency is remarkably high, being not far short of 100 per cent., so that a thickness of 0·00002 in. of platinum may be deposited in about 4 minutes.

Temperature.—The recommended bath temperature is between 65° and 80°C.

The high cost of platinum largely precludes its use as an anode, although no better material could be employed for the purpose. However, platinum-plated copper sheets have been found quite satisfactory in lieu of solid platinum.

MAINTENANCE OF ELECTROLYTE

The platinum anodes are insoluble and therefore the metal content must be maintained by addition of the platinum salt. The caustic soda content must also be maintained owing to carbonation as time goes on.

The preparation and finishing of the articles before and after plating, follow normal procedures, except that it is important to note that where cyanide is used in the preparatory stages of cleaning, it must be thoroughly removed from the articles before immersion in the platinum bath. Small quantities of cyanide cause patchiness of the deposit, and in any quantity at all, deposition may cease completely. In drying out the work after plating, a drag-out container is necessary in order to conserve the platinum electrolyte adhering to the work, and this should contain distilled water, the resultant solution being used for make-up purposes.

The alkali platinate electrolyte is not only highly efficient cathodically, but it is possible to build up remarkably thick deposits in it. For example, it has been claimed that heavy deposits up to 0·1 in. in thickness are obtainable. It is estimated, however, that a 5-minute plate equivalent to 0·000025 in. deposit is sufficient for most purposes, particularly when an underlying deposit has first been applied. Nickel represents a useful undercoating, and it is particularly necessary whenever lead, tin, or zinc alloy articles have to be plated.

The hardness of deposited platinum makes it remarkably resistant to wear, as the following tests quoted by Davies and Powell indicate. These tests were carried out on a continuous belt machine, using an unwashed flannel belt travelling at 600 feet per minute, the test pieces being plated nickel silver teaspoons loaded with 100 grams on the bowl. The average time required to cut through the respective deposit was as follows : —

Silver plate 0·0012 in. thick	20 hrs.
6 minute platinum plate (0·00003 in.) ...	20–25 „
Silver plate 0·00008 in. thick	8 „
4 minute platinum plate (0·00002 in.) ...	8 „
Silver plate 0·00004 in. thick	0·75 „
2 minute platinum plate (0·00001 in.) ...	2 „

PALLADIUM PLATING

Recommended baths for the deposition of palladium may be found in some of the earliest records in the literature; thus, for example, Smee, in his book "Electrometallurgy" published in 1841,(8) mentions palladium nitrate as an electrolyte, and in 1843 recommends an ammoniacal solution of ammonium palladium chloride.

Various other solutions were proposed from time to time but it is interesting that as late as 1899 Cowper Coles(9) advocated a palladium ammonuim chloride solution dissolved in an ammonium chloride solution.

It is doubtful whether any of these solutions were of any direct commercial application, and it was not until Keitel and Zschiegner paralleled their work on platinum by using an ammoniacal solution of dinitro-diammino palladium that an electrolyte was produced capable of continuous plating, the same problem of avoiding accumulated inert salts being thus largely solved.

Powell and Davies proposed two types of bath, the first comprising a solution of palladosammine compounds, *e.g.*, chloride, sulphate, etc., and the second from electrolytes containing soluble complex nitrites in either neutral or slightly acid solution.

Two types of processes represent the most recent attempts at depositing the metal commercially. They are, respectively, (*a*) a soluble anode process, and (*b*) a palladium-ammine diaphragm process. The first is due to A. R. Raper(10) and the second to R. H. Atkinson,(11) both in association with the Mond Nickel Company Limited.

SOLUBLE ANODE PROCESS

The main constituent of the electrolyte used in this process is an alkali complex nitrite of palladium. To this is added a soluble chloride or bromide. A suitable solution is the following:—

Sodium palladium nitrite $Na_2[Pd(NO_2)_4]$ equivalent to 10 grams of palladium.

Sodium chloride 30 grams.

Water 1 litre.

The nitrite salt is prepared as follows:—

Starting with metallic palladium, this is completely dissolved in aqua regia. The solution is then evaporated to dryness and again re-evaporated, using concentrated hydrochloric acid in order to produce the chloride of palladium and also remove any nitric acid. This is then dissolved in about four equivalents of aqueous sodium

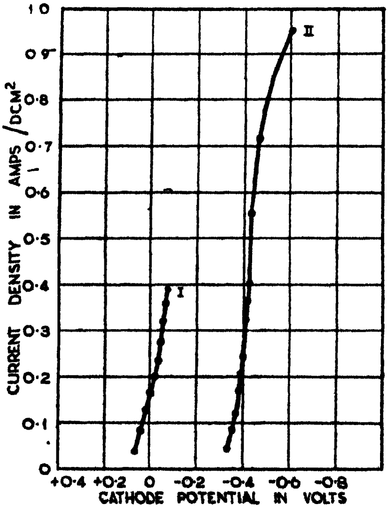

Fig. 54.—Cathode potential/current density curves for soluble anode and palladosammine processes respectively. (Due to Atkinson and Raper J. Electrodepos. Tech. Soc., 10-1, 8, 1933).

nitrite solution, and on heating to boiling the following reaction takes place :—

$$PdCl_2 + 4NaNO_2 \longrightarrow Na_2[Pd(NO_2)_4] + 2\ NaCl.$$

The resultant solution thus already contains sodium chloride, which may be readily calculated, and the balance is added in accordance with the formula given above. After filtering, the solution is ready for plating purposes. This undoubtedly provides a simple method of preparing the electrolyte, which could be carried out readily in any laboratory or plating shop.

CONDITIONS OF OPERATION

The current density employed is not very high and is of the order of 1 amp. per square foot. On the other hand, the cathode efficiency is very high, practically 100 per cent.—as is also the anodic current efficiency, pure palladium being used as an anode material. The latter should be 99·9 per cent. purity, preferably, and while cast or hard-rolled plates may be used. it should preferably be hard-rolled. Atkinson and Raper report that soft annealed palladium disintegrates too rapidly, and that in preference, the anodes should be bagged, since a certain amount of disintegration does occur during working. The optimum temperature of the solution is about 40°C. to 50°C.

The *p*H of the solution when first prepared is about 5, and gradually rises as the electrolyte is worked. Eventually the electrolyte attains a slight alkalinity, the *p*H actually having risen to approximately 8·0. Nevertheless, no noticeable changes appear to take place in the appearance of the deposit, and *p*H therefore does not appear to be a critical factor.

PROPERTIES OF THE DEPOSIT

This process is normally used to deposit thickness of the order of 0·0001 in. or less, and it cannot be used for building up thicker deposits, since cracks appear, due, presumably to the high stress present in the deposit as a result of hydrogen occlusion. The deposits are very bright and normally require no polishing after deposition.

The comparative thinness of the deposit makes it essential to cover the basis metal with a corrosion resistant deposit before palladium plating; this can be copper, nickel or silver, and the thickness of these deposits should be such that adequate corrosion resistance is imparted. The palladium deposit is, in effect, a veneer to protect the underlying deposit—normally silver, which is thus prevented from tarnishing in service. Silver is particularly desirable as an immediate undercoating to palladium, in that the latter metal may be more readily stripped from silver than most base metals.

DIAPHRAGM PROCESS

In this process a porous pot diaphragm is employed in order to prevent the anolyte and the catholyte from mixing. It is thus not as straightforward in regard to plant requirements as the soluble anode process, and this would probably militate against its development industrially. On the other hand, it is possible to plate at considerably higher current density, while the cathode efficiency is also very satisfactory over a wide range of temperature and current densities. The current efficiency actually increases with increase in current density, and at 20 amps. per square foot reaches 100 per cent.

The type of cell employed is illustrated in Fig. 55. In this (A) represents a wooden cell with two partitions (P) in which there are windows (W,W.) of thin porous tiles of Leclanché porosity. The cell is lined with rubber, which covers the wooden partitions. The two anodes (B) are of lead. The catholyte is placed in the centre with the cathode centrally disposed in this compartment and the anolyte on each side of the central cell. The catholyte is prepared as follows:—

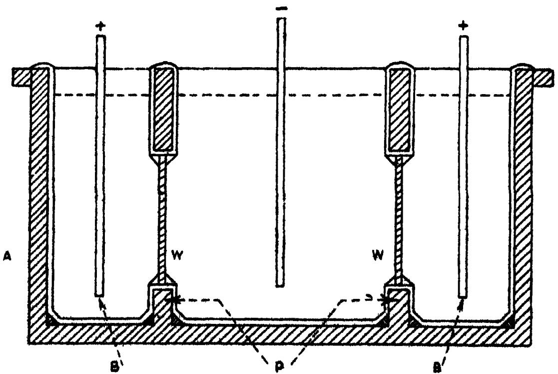

Fig. 55.—Details of cell used in diaphragm process for paladium plating (Due to Atkinson and Raper, " J. Electrodepos. Tech. Soc.," 10-1, 8, 1933)

Palladosammine chloride is first prepared from pure palladium sponge by dissolving in aqua regia, evaporating to a pasty consistency, moistening with hydrochloric acid and evaporating until no further brown fumes are given off. This produces palladium chloride, which is then dissolved in dilute hydrochloric acid, and heated to 50°C., and excess of ammonia added until a colourless solution is formed, which is cooled and acidified with HCl. The precipitated palladosammine chloride is then filtered off and washed.

This salt is not very soluble, and has now to be converted into the tetrammino compound as follows:—

For each litre of catholyte, 40 grams of palladosammine chloride in 35 cc. of 0·880 ammonia is dissolved, and 10 grams of ammonium chloride are then added and made up to one litre with distilled water.

As for the anolyte, this is produced by dissolving 10 grams of ammonium carbonate and 20 grams of ammonium sulphate in water. To this, 50 cc. of 0·880 ammonia are added, and the resultant solution made up to one litre with water.

CONDITIONS OF OPERATION.

A current density of the order of 10 amps. per square foot may be employed. Excessive voltages are not required, despite the diaphragm, as the voltage drop across the latter is not much more than about 0·1 volt. For an electrode distance of 20 cms. not more than 2·5 volts is required to produce the desired current density. The current density to give the optimum results varies with the metal content of the catholyte. The solution as produced above would contain about 20 grams of palladium, and a temperature in excess of 40°C. would give good results. It should be noted, however, that higher temperatures are not conducive to the production of the brightest deposits.

With regard to the anolyte, one important practical consideration which must be noted is the fact that it is possible to form nitrogen trichloride in the absence of ammonia, and the latter is extremely explosive. Atkinson and Raper point out, however, that, provided the anolyte smells of ammonia, there is no danger of forming this compound. The anolyte, however, requires replenishment from time to time in order to remove excess ammonium chloride.

The diaphragm process has the one important advantage over the soluble anode process, in that it is possible to build up thick deposits, and as much as 0·01 in. has been built up by these means, although these thicker deposits tend to be brittle. Bright deposits are obtainable up to a thickness of 0·00002 in., but lose some of their brightness thereafter. It has been stated that a thickness of 0·0001 in. is necessary to overcome porosity, but although this is a relatively thin deposit compared with practice in the deposition of the base metals, it is nevertheless too thick to contemplate as a commercial finish except on the most expensive articles.

Whatever deposit is applied to the base metal to ensure corrosion resistance, for example, nickel or copper plating, an immediate undercoat of silver is desirable, in that palladium, as already mentioned, may most successfully be stripped from a silver surface. This is carried out by making the component the anode in an electrolyte containing the following constituents :—

Hydrochloric acid	3.6 grams.
Sodium chloride	100 grams.
Water	1 litre.

On the other hand, nickel or copper immediately under palladium will be pitted and badly corroded during the stripping process, and other methods of removing the palladium are then necessary. Possibly the simplest way is to buff the deposit off.

Precious metal deposits are likely to find their greatest sphere of application in the finishing of luxury type articles, and the deposit is therefore of special interest to the jewellery industry. It is particularly useful as a finish on silver and silver-plated components to prevent tarnishing of the latter metal, but in this respect it meets a formidable competitor in the rhodium deposit, which has a whiter and more pleasing appearance than palladium. Comparatively thin deposits are quite reasonably abrasion resistant and stand up satisfactorily to ordinary wear in service.

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CHAPTER XI.

Deposition of the Precious Metals—Rhodium

UNDOUBTEDLY the most interesting metal in the platinum group from the depositor's point of view is rhodium, and prior to the war considerable steps had been taken not merely in its development in the laboratory but in its wide-scale use industrially.

The difficulties attending the deposition of rhodium on a commercial scale were considerable, one of the most formidable being the incorporation of the metal in a suitable electrolyte. This arises from the remarkable resistance of rhodium to chemical attack, exceeding as it does the comparative inertness of platinum itself in this respect. It thus proves correspondingly difficult to dissolve in solution. In consequence, comparatively few solutions are available for its deposition, and the manner of their preparation is of such importance that full data covering this aspect of the subject will be given in due course.

The properties of rhodium which make it attractive have already been broadly indicated. In brief, they are: (1) the truly stainless character of rhodium; (2) the beauty of the metal, which is the whitest in the platinum group and not far removed from silver in colour; (3) comparatively high reflectivity; (4) resistance to oxidation even at high temperature; and finally (5) comparative hardness.

The big economic drawback, of course, is cost, but it is a remarkable and also a fortunate thing that very thin coatings of the metal fully impart to the surface of the basis metal the properties and characteristics of the deposit, and this applies particularly to corrosion resistance. Thus, Atkinson and Raper ([1]) record the fact that a coating of rhodium not more than 0·0001″ thick, deposited on a silver vase, was successfully able to withstand the action of boiling concentrated *aqua regia* for 30 minutes without loss of weight or, in fact, in any way changing in appearance.

ELECTROLYTES

The first references to the electrodeposition of rhodium appear to occur in the literature of 1891. In that year, Joly and Leidié ([2])

made use firstly of a solution of a double chloride of rhodium and an alkali or ammonium chloride, and, secondly, a sulphate solution, the rhodium being fused with potassium bisulphate. In that year also, E. F. Smith (³) used a solution containing sodium rhodium chloride, sodium phosphate and phosphoric acid, having found that the double cyanide of rhodium and potassium could not be used for depositing the metal. The deposit obtained, although quite compact and adherent, was dark in colour.

An American patent for depositing rhodium appeared in 1912 (⁴). The patentee, Marino, used a solution containing sodium rhodium chloride, adding magnesium boro-citrate as a reducing agent, other addition agents also being advocated.

In 1927, Zschiegner took out a patent (⁵) covering an ammoniacal aqueous solution of the reaction product of rhodium chloride with sodium nitrite, this being presumed to form an ammino-nitrite of rhodium. Three years later Keitel (⁶) patented an improvement on the process, claiming that contaminating products did not form in the electrolyte, and continued deposition was therefore entirely practicable. However, these solutions were not suitable for commercial use, and Atkinson and Raper (¹) considered that the reason for this was that the " sparing solubility of the plating salt and the low current efficiency, even when operating at 90°C., spoiled what was otherwise a promising idea." The view of K. Schumpelt (⁷) in this connection is interesting, as in commenting on the patents which were issued for rhodium plating solutions covering the double nitrites in acid or alkaline solutions, rhodium sulphate or chloride in combination with corresponding aluminium salts and free acid, and rhodium ammonia-cyanides, he states that it is only from acid electrolytes that it is possible to obtain brilliantly white deposits and at the same time to achieve good throwing power. Accordingly, the solutions which, he states, have been most successful in America are of the acid type, utilising rhodium sulphate dissolved in dilute sulphuric acid or phosphoric acid, or a rhodium phosphate in combination with the same acids.

This seems to accord with the statement of Cinamon (⁸) who, earlier in 1932, stated that only two types of electrolyte were in general use, namely, the sulphate and the phosphate. In 1934, an American patent by F. Zimmerman and H. E. Zschiegner (⁹) appeared, which claimed the use of a complex rhodium phosphate in acid electrolytes, and, according to Schumpelt, this is the basis of practically all the rhodium plating solutions in use in America and Canada

COMPARISON OF SULPHATE AND PHOSPHATE ELECTROLYTES

The difficulty of bringing rhodium into solution to form a suitable electrolyte is one which, in the early days, stood in the way of developing a practical process which could be operated on a commercial scale Drastic means have to be employed to cause rhodium to become active For example, it may be fused with low melting metals, such as lead, zinc and bismuth, or with combinations of these base metals, the latter being dissolved out, thereafter leaving finely divided rhodium, which is more susceptible to solution in acid Alternatively, the finely divided rhodium, if intimately mixed with sodium chloride and heated to redness in a silica tube through which moist chlorine is meantime passed, produces sodium rhodium chloride

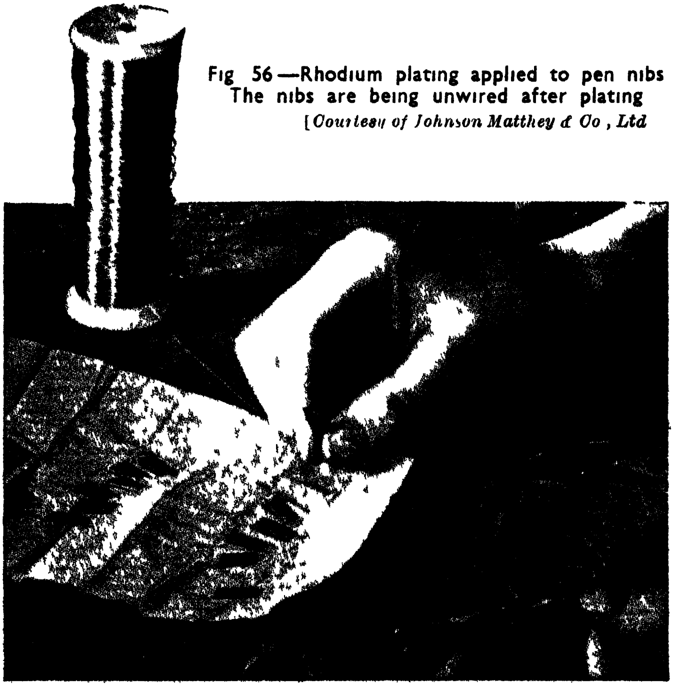


Fig 56—Rhodium plating applied to pen nibs The nibs are being unwired after plating

[*Courtesy of Johnson Matthey & Co , Ltd*

However, it is the sulphate and phosphate baths which have been most successful in the deposition of the metal, although Cinamon(10) claims that he obtained fair deposits from tartaric acid electrolytes. In investigating the relative merits of sulphate and phosphate baths, Cinamon holds that the phosphate bath produces a much more attractive soft white colour in the deposit, which is "full of life" and "has the exact tone or shade of a diamond," this comparison arising from the fact that rhodium was very largely used in the jewellery industry, *e.g.*, on platinum rings, trinkets, brooches, etc., where the deposit is seen cheek by jowl with precious stones. As against this, the sulphate solution is easier to manufacture, and also possesses somewhat higher conductivity, thus requiring less platinum anode area for deposition and a lower voltage, while it is also speedy in action. The phosphate solution, on the other hand, requires higher voltages, of the order of 7 to 10 volts, and rather longer periods of deposition. It can, however, be operated at relatively low temperatures, *e.g.*, 85°F. to 100°F., while the spray produced at the cathode is non-injurious. As against this, the sulphate bath has to be worked at a high temperature, *e.g.*, about 175°F., and the spray given off is decidedly plentiful, so that acid-exhaust equipment is necessary to prevent it getting into the shop atmosphere.

It is a curious thing that the colour of the rhodium deposit varies quite definitely with the metal content of the solution in the case of the phosphate bath, and this provides a ready means of checking the rhodium content, indicating replenishment when necessary. This, however, does not apply to the sulphate baths, the deposits from which have a somewhat blue cast and are not so white.

PREPARATION OF PLATING SOLUTIONS

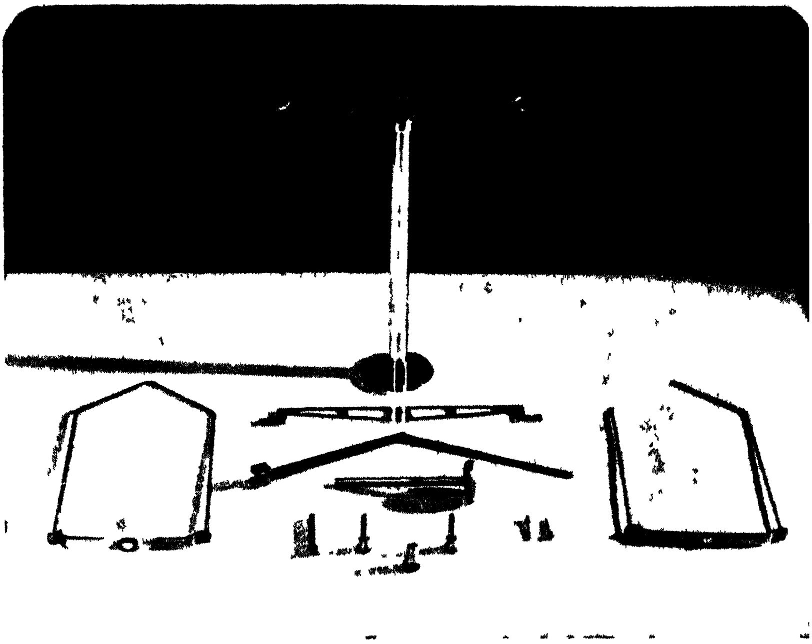
According to Atkinson and Raper,(1) the simplest method of producing the plating salts, *e.g.*, the sulphate, is either to fuse the finely divided rhodium metal with potassium bisulphate, or to produce sodium rhodium chloride in the manner already indicated above. Either of these salts may then be dissolved in water, and the solution heated to 80°C. Thereafter, caustic soda solution is added until faint alkalinity is perceptible, the rhodium being then completely precipitated as a yellow hydrate. This is then washed free from dissolved salts, and can then form the sulphate by dissolving in sulphuric acid. The corresponding salts, *i e.,* chloride, phosphate, may similarly be formed by dissolving in hydrochloric and phosphoric acids respectively.

These authors favour an electrolyte based on ammonium rhodinitrite, obtained by treating sodium rhodium chloride with sodium nitrite and then adding ammonium chloride. The ammonium rhodinitrite is then fumed down with concentrated sulphuric acid and diluted with water to form the electrolyte. At a comparatively low current density—about 5 amps. per square foot, and a temperature of 40°C., it is claimed that very bright, practically pore-free deposits are produced.

For those who prefer to make up their own salts direct from the metal rhodium, very full details are given by Cinamon in one of his papers.(11) The method is given below, it being assumed that as a unit, 2 oz. of rhodium metal are employed in the first place.

Using the fusion method mentioned above, 20 oz. of lead are mixed with the rhodium, together with a little sodium bicarbonate and borax. The mixture is placed in a sand crucible and heated in a gas air furnace until the reaction ceases and there is a mirrorlike appearance on the top of the melt. The heat is applied slowly for five minutes to avoid cracking the crucible, and thereafter a full flame is used for 15 minutes. The melt is then rapidly transferred into an iron mould, greased with a little oil inside and then allowed to cool until solid, after which the mould and melt are plunged into cold water. The button formed is removed, washed and heated in dilute hydrochloric acid (50 ccs. HCl in 500 ccs. of water) for a period of two to three hours, the flux dissolving as a result of this process, or being sufficiently softened to be removable mechanically.

The button is now placed in a six-litre porcelain evaporating dish and four litres of water together with one of nitric acid, are added, the whole being heated until the button has completely dissolved. The supernatant liquor is now decanted, this containing all the lead, and the precipitate filtered and washed until a test with chromate reveals lead to be absent. The precipitate is now transferred to a two-litre Erlenmeyer flask and 100 ccs. of water added, the whole being stirred, 300 ccs. concentrated sulphuric acid being added meanwhile. The solution is now heated slowly, and after this it is allowed to stand until completely cooled. The solution now contains rhodium sulphate, and is put into two two-litre flasks, each



[*Courtesy of Johnson Matthey & Co, Ltd*

Fig. 57.—Balance parts which have been rhodium plated for both decoration and corrosion resistance. Rhodium deposits have very high resistance to chemicals

containing one litre of cold water. On allowing to stand, a greyish-white precipitate separates, which is a combination of lead sulphate and undissolved rhodium. The solution is now filtered and the precipitate washed free from rhodium. Ammonia is added to the rhodium solution in small quantities, until the rhodium is completely precipitated. The supernatant liquid is now drained off, and the precipitate is repeatedly washed very carefully until it is free from sulphates; rhodium hydroxide is thus produced and is ready for conversion into sulphate or phosphate electrolytes.

RHODIUM SULPHATE

To convert into rhodium sulphate, 4 ccs. of sulphuric acid are added for every gram of original rhodium, and heat is applied slowly, because of fuming, until complete solution takes place. This may be a slow process, but, thereafter, one litre of distilled water is added and the solution is cooled, filtered, and washed until no red colour is evident in the wash waters. The finished rhodium sulphate solution is then ready for plating.

RHODIUM PHOSPHATE

To obtain this electrolyte, 8 grams of phosphoric acid are added for every gram of original rhodium. Again, the solution is slowly heated until the rhodium is completely dissolved, and one litre of distilled water is added, any precipitate being filtered. The filter is cooled, and having been brought up to the original volume, the solution is ready for plating.

COMPLEX RHODIUM ELECTROLYTE

According to Schumpelt,(7) rhodium sulphate may be dissolved in dilute sulphuric acid, or phosphoric acid may be used, and also vice versa, *i.e.*, rhodium phosphate may be dissolved to form a bath containing sulphuric acid. The advantage of rhodium sulphate over rhodium phosphate is that the former produces a well-defined compound, the formula of which is $Rh_2(SO_4)_3$ $12H_2O$, whereas there are many phosphates, the chemical formulae of which are so complex (while some of them also are not too stable since they undergo changes or are apt to decompose) that it is difficult, if not impossible, to identify them.

A bath favoured by Schumpelt is one containing 2 grams of metallic rhodium per litre in the form of a complex phosphate, which is then dissolved in a 2 per cent. sulphuric acid solution. This electrolyte is contained in a tank constructed of some inert material to prevent contamination, glazed earthenware being particularly suitable for the purpose. Such a solution can be operated at ordinary room temperature, but it may be heated (by means of a water jacket) up to, say, 60°C. The current density is of the order of 20 amps. per sq. ft., but deposits can be produced at considerably higher current densities, it being possible to employ up to 100 amps. per sq. ft. The electrolyte produces a deposit which is very bright and requires no subsequent buffing. Components of complex shape can be readily coated with rhodium, as the throwing power is extremely satisfactory and, in fact, almost equal to that obtained in a silver cyanide electrolyte.

It would appear that there is some divergence of view between

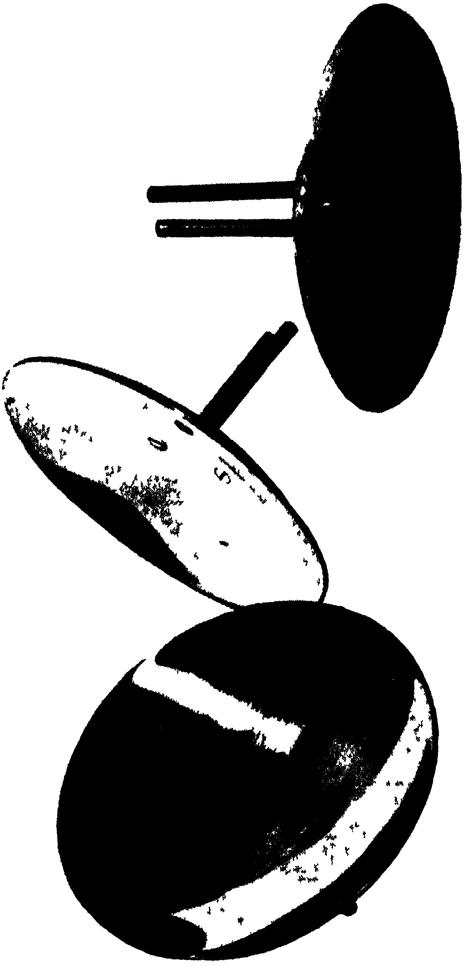


Fig. 58.—Application of rhodium to metal reflectors. The reflectors are thus rendered tarnish proof.

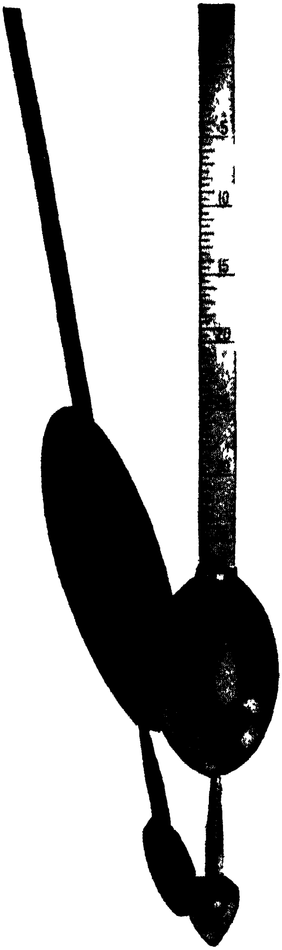


Fig. 59.—Application of the rhodium deposit to metal hydrometers, whereby the latter are rendered highly corrosion-resistant

[*Courtesy of Johnson Matthey & Co., Ltd.*

different authors as to the relative merits of the phosphate and sulphuric acid types of electrolyte respectively. Thus, while Cinamon's view is that it is the phosphate bath which produces the more attractive rhodium deposit, Schumpelt considers quite definitely that the bath based on a phosphate solution, *e.g.*, by dissolving a complex rhodium phosphate in phosphoric acid, has a tendency to produce deposits which become foggy and dull round the edeges. He instances a test where two deposits were obtained respectively from sulphuric acid and phosphoric acid type electrolytes, the same weight of rhodium being deposited in each case. This was equivalent to 0·2 milligrams per sq. in. After plating, the samples were submitted simultaneously to an atmosphere containing 2 per cent. moist hydrogen sulphide. As a result of this test, the strips plated in the sulphuric acid electrolyte were found to have withstood the tarnishing action better than those which had been plated in the phosphoric acid electrolyte. It is not, however, clear why this should have occurred, since it appears unlikely that there would have been a marked difference in porosity as between the two types of deposit, considering the thinness of metal applied in either case.

According to Cinamon, rhodium sulphate solutions should be worked at a concentration as low as one gram of metallic rhodium per litre, while the sulphuric acid content can vary considerably over a range of from 4 to 40 grams per litre, the best plating results being obtained round about 80°C. Nevertheless, Cinamon agrees that it is also possible to plate successfully at low temperatures, *e.g.*, room temperature, with correspondingly low current densities, *i.e.*, of the order of 10 to 15 amps. per sq. ft. It is, however, possible at the higher temperatures to employ as much as 200 to 300 amps. per sq. ft. with corresponding reduction in the time of plating. Under such conditions, ten seconds is sufficient to obtain an adequate deposit, while fifteen seconds will show a tendency to burning. This author recommends a somewhat higher concentration of rhodium for the phosphate solution, namely, 2 grams of rhodium and 30 grams of phosphoric acid per litre. Temperatures varying from room to 45°C. may be employed, the higher range enabling faster deposition to take place.

The corresponding current densities for varying temperature conditions are as follows: At 25°C. the current density employed is approximately 70 amps. per sq. ft.; and under these conditions, a deposit of one milligram per sq. in. is produced within two minutes. When the temperature is increased to 35°C., the rate of deposition is doubled, and at 45°C., increased to four times the speed of deposition at 25°C. A better colour of the plate is obtainable at the lower temperature.

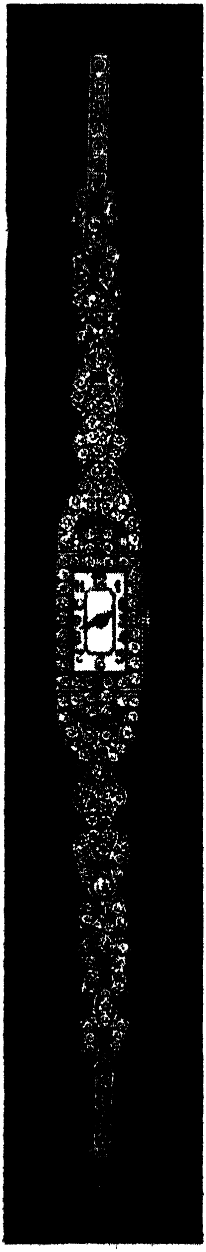


Fig. 60.—Rhodium-plated platinum bracelet

The difficulty arising from the lower conductivity of the phosphate solution may, to some extent, be countered by addition of sulphuric acid to this bath. Thus, by addition of some 5 grams of sulphuric acid for each gram of metallic rhodium present in the solution, the voltage required may be reduced from 7 –10 volts down to 4—6 volts.

While the question of colour of the rhodium deposit has exercised the jewellery industry in particular, and has been ascribed to types of electrolyte employed, it is probable that this property is affected to quite an appreciable extent by the contaminants which enter the bath, thus falling into line with observed phenomena in bright plating practice generally, several instances of which have already been indicated in earlier chapters.

Cinamon, in fact, has made some study of the effect of various ions on the appearance of the deposit; thus, a very slight trace of ammonia has been found to improve the whiteness of the deposit where this has been falling off as a result of continued working of the bath. On the other hand, an excess of ammonia is deleterious. Again, the sodium ion was found to be particularly detrimental, as in almost any small amount it was sufficient to affect the colour of the deposit. A small amount of calcium, on the other hand, was found to be beneficial, but if present in excess affected the colour badly. Apparently a similar effect occurs as a result of the presence of lead, since it was found that sulphuric acid of high purity, present in a sulphate type bath, did not produce such good colour as one in which a lower purity acid was employed containing a slight trace of lead. On the other hand, if lead was present beyond a

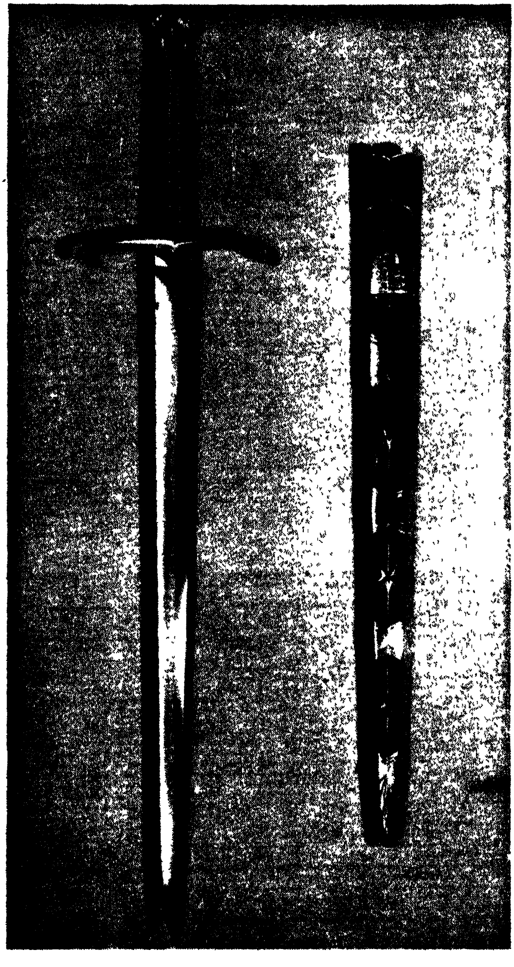


Fig. 61.—The Stalingrad Sword. The lockets and chapel and the scabbard of the Stalingrad Sword were very skilfully chased in silver by Mr. L. G. Durbin, M.V.O., and subsequently rhodium plated to bring out the beauty of the design. The Inscription on the plate is as follows:—

"To the steel-hearted citizens of Stalingrad, the Gift of King George VI, in token of the homage of the British people."

Craftsmen may be interested in the following further details of this superb piece of work.

The red stars between the lockets are red enamelled and silver-gilt with gilt tooling in the red leather background. The coat of arms, crown and cypher are in gold. The blade is, of course, in steel, etched and engraved with the inscription. The Quillons are of silver with silver-gilt Leopards' heads at each end. Two red enamelled bands come at each end of the grip, which is bound with twisted gold wire; the Pommel is made of carved crystal. The Sword is the work of a team of eighteen craftsmen co-ordinated by a Committee of the Goldsmiths' Company.

[*Courtesy of the Goldsmiths Company*

certain concentration, the effect was found to be deleterious again. All this indicates how sensitive the bath is to small impurities and how essential it is to take every possible precaution to prevent foreign ions from entering the solution.

In this connection, the nature of the basis metal of the components to be rhodium plated is not unimportant. Fortunately, nickel and silver have been found to be two of the safest deposits to apply to articles prior to rhodium plating, in that they have proved to be reasonably neutral in their effect on the colour of the deposited rhodium. Rhodium does not readily deposit on certain metals, as, for example, ferrous metals such as iron and stainless steel, or lead, tin, cadmium, chromium or zinc base die-castings. Apart from silver and nickel, the precious metals, platinum, palladium, gold, etc., readily receive a rhodium deposit, as also do copper and nickel-silver. Alloys such as zinc base die-castings which would be attacked in the acid electrolytes, particularly the sulphuric acid bath, must obviously be thoroughly sealed off by first depositing a layer of copper, preferably followed by either nickel or silver.

The cost of rhodium is such that obviously it would be entirely uneconomic to deposit more than a very thin coating of the metal. While it is astonishing how well such a thin deposit, which may not be more than 0·000005 in. may withstand atmospheric conditions and even light abrasion in service, the deposit cannot be considered to be completely free from pores; hence a rhodium-plated surface may show attack if left untended when exposed to the atmosphere, particularly under industrial conditions. This attack may take the form of minute white local spotting, and it can readily be removed periodically, the initial rhodium finish being then largely reproduced. In point of fact, this unsightly surface effect can be completely obviated if the surface be cleaned occasionally, and in this respect the rhodium finish is very similar to the chrome deposit. It is perhaps not as widely realised as would be desirable that chromium plating while undoubtedly itself tarnish-proof will nevertheless tend to deteriorate superficially if left to itself. In the case of chrome, there is a similar spotting effect except that discoloration is brown rather than white, and chrome should undoubtedly be carefully cleaned periodically to maintain its initial lustre.

Rhodium plating so far has been most largely used in the jewellery industry. Its costliness makes it possible to use the deposit as a finish for the most expensive jewellery, not merely silver and white gold, but also platinum itself (see Fig. 60). Undoubtedly the appearance of the latter metal is much enhanced by the deposited rhodium, platinum normally appearing somewhat dull grey and semi-lustrous in comparison. The thickness which is normally deposited does not usually exceed 3 milligrams per sq. in., *i.e.*, 0·000015 in.

Besides jewellery and silverware, rhodium has been found to be a valuable metal to deposit on reflectors of many types. As an instance of this application, one of the largest stages in New York was equipped, as long ago as 1931, with several thousand rhodium-plated reflectors. It has also been applied to cinema projector reflectors and has proved to be very satisfactory in service. Carbon particles, from the arc used in proximity with the reflector, may be readily removed where they fall on the rhodium surface without leaving any trace.

One difficulty with regard to rhodium deposits is that associated with the stripping of defective plating, owing to the fact that rhodium is so insoluble in practically every chemical reagent which has been tried. While the metal itself cannot therefore be attacked, the most hopeful method of stripping is based on the fact that it is to some degree porous, and therefore it is possible to attack the undercoating, which then lifts the rhodium. Where the undercoating is silver, it may be possible to strip the rhodium by making it the anode in a chloride or hydrochloric acid solution. Sodium cyanide electrolyte has also been recommended for this purpose. However, the stripping is by no means clean under almost any circumstances, and while as much as possible of the deposit may be removed by electrochemical means, eventually mechanical treatment or buffing has often to be resorted to in order to reach the basis metal uniformly.

Rhodium plating is undoubtedly one of the most interesting of deposition processes, and it is a tribute to those who have taken part in the intensive research work which has been necessary to attain the results possible to-day, that it has in a short time attained such considerable industrial importance. There can hardly be any doubt that it will be increasingly used in future when the necessary material is more freely available.

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CHAPTER XII.

Electrolytic Polishing of Carbon Steels

THUS far, we have dealt with the most important applications of electrolytic polishing, covering (*a*) those metals which have already received a fair degree of industrial application, and (*b*) metals which although their development in this respect may lag far behind the former class, nevertheless show promise that in time they may advance to the point of commercial application. The most important metals in the first class are the austenitic steels, aluminium, nickel, brass, and perhaps, silver; while in the second, there are, as promising possibilities, the base metals, copper, zinc, tin, and especially carbon steels.

Consideration has been given to a related technical development in the electrolytic field, namely, the production of bright electrodeposits. Both these technical developments are aimed at approximately the same objective, namely, the reduction or elimination of mechanical polishing operations, and it is perhaps correct to state at this acute moment in our national existence that never have processes of the type dealt with been so important to so many of the metallurgical industries as they are to-day. There are many reasons for this, but it is not proposed to enter here into the economics of the situation which now confronts the metallurgical industries in general, and the metal finishing industries in particular, in this connection. It is sufficient to indicate that manual polishers are most difficult to obtain to-day anywhere, and unless a new class of polishers is brought into being by training, industrial executives are likely to be left with many thorny problems in the near future.

What then are the possibilities of electrolytic polishing replacing some, at any rate, of the mechanical methods employed hitherto? The answer to this question is bound up with the effort which industry is prepared to put into further development and research. Such research will be well worth undertaking, in that some of it may rapidly enable the electro-chemist to pass from the threshold of the laboratory to the workshop. In the author's view, it would be foolish to say that the prospects are of a roseate character, but at any rate they are promising to a greater or less degree, according to the problem which requires to be faced. There is no question that many important advances will occur in this field in the next few years, and it is not improbable that some of them may be distinctly startling in their effect on the polishing industry.

CARBON STEELS

Undoubtedly one of the problems which it would be most desirable to solve would be the perfection of tried and proved methods—not merely practical but also readily controllable—for electropolishing that class of ferrous metal which comes under the category of carbon steel. Not only does this class cover a very considerable field of raw material entering so many manufacturing operations, but it is also material on which it is difficult to obtain an adequate polish by mechanical means. The vista which is opened up by a successful solution of the problem on a big scale is obvious, and the possibility of starting with steel as a basis material, electrolytically polishing the surface, and thereafter bright plating, so that all mechanical polishing is eliminated, is one which would obviously lead to very wide application were it feasible.

One of the crucial difficulties lies in the considerable effort which is required to bring up an ordinary carbon steel surface to a fair polish. This varies with the type of steel and the heat treatment which it has undergone, but normally not less than two or three grinding or polishing operations are found to be necessary to achieve any degree of polish at all. It may be, therefore, that if some of this drudgery can be eliminated, electrolytic polishing may yet find an application in the later stages of polishing. As with other base metals, a combination of mechanical and electrolytic polishing may supply the first fruits of the labours of the research worker.

It is, of course, fairly well known that it has already been possible to polish electrolytically, carbon steel surfaces of small area. Thus, P. A. Jacquet(1) and P. Rocquet(2) reported that steels of various types (excluding the stainless variety), as well as armco iron, could be polished in a solution of the following composition:—

Perchloric acid (density 1·61)	185 ccs.
Acetic anhydride	765 ccs.
Distilled water	50 ccs.

A voltage of the order of 50 is required to produce a current density of 4 to 6 amp./sq. dm. The temperature of the solution was not allowed to exceed 30°C., and moderate agitation was employed. The time of electrolysis was 10 to 15 min., and the specimen after treatment was usually washed in running water, after a short immersion in a dilute acetic acid solution.

METALLOGRAPHIC APPLICATION

As already indicated, the purpose of producing the electrolytic polish on the ferrous materials named was purely metallographic, the electrolytic polishing replacing mechanical methods which are normally employed before etching the section for subsequent micrographic examination.

While this application is of considerable importance to metallurgists, there would be obvious difficulties in translating a process such as that described by Jacquet and Rocquet into industrial practice, where the polishing of articles of comparatively large area and considerable variation in shape is involved. Nevertheless, the methods used for metallographic applications produce a very high polish and indicate that possible adaptations of this or similar processes cannot be completely ruled out.

Some years ago, a valuable Symposium was held by the Metals Division of the A.I.M.E., in America, on the subject of Metallographic Polishing Methods, and a considerable amount of information is available in a report on the proceedings which appeared in the *Iron Age*(3). Fig. 62 shows the apparatus which was used by the United States Steel Corporation, in polishing steel specimens for metallographic examination. It consists of a vessel which contains the electrolyte immersed in a cooling bath, cracked ice being the cooling medium. The cathode, which is made of aluminium sheet, surrounds the anodic specimen, which is centrally disposed. Although the cathodic area is very much greater than the anode, no observable detrimental effect appears to arise, even though the area of the cathode may be as much as 30 times that of the anode; neither, apparently, does its position with respect to the anodic specimen affect the quality of the final polish. Normally, a distance of about one inch is employed between the specimen to be polished and the cathode. The specimen must, of course, be first freed from traces of grease, and any scale is ground off before

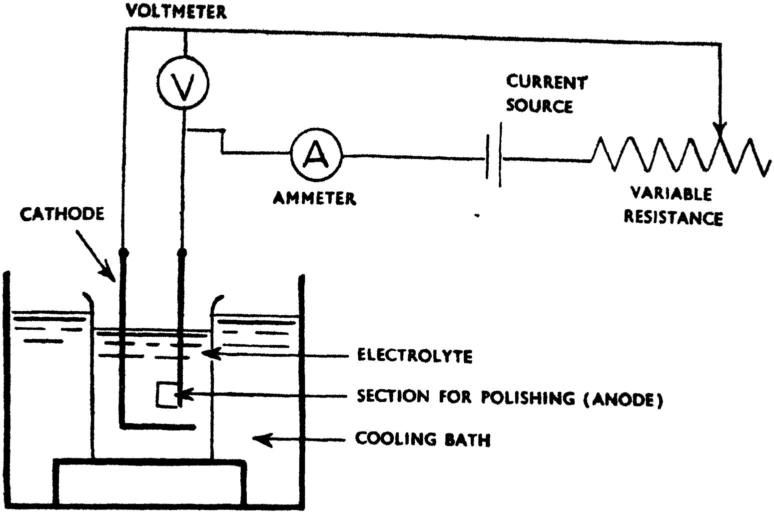

Fig. 62.—Typical circuit and apparatus for electrolytic polishing (metallograph application).

it is placed in the electrolyte. The solution used is of the type proposed by Jacquet.

An interesting contribution by J. R. Vilella, to the Symposium, recommends the following sequence of operations. First, the surface of the sample is ground down to a grit of 500 mesh, or finer. It is then degreased, attached to the positive side of the electrolytic circuit, and immersed in the solution. A carefully calculated current is then applied, which has been determined by previous experiment to produce a high polish. At first the current begins to fall off and the voltage to rise, and at this stage the surface of the steel specimen shows discolouration; thereupon, the current is adjusted in order to maintain the previously calculated current density and it then remains constant while the electrolytic polishing action takes place. Thereafter, the anode is washed and dried, and is found to be in a highly polished condition, ready for etching.

Probably the most important factor in producing good polishing results is the correct alignment of the current density, and this is best determined by trial. Usually it is found that if the current density is too low, the anode is apt to be seriously attacked by the electrolyte, with resultant dissolution and etching of the surface. If, on the other hand, it is pitched too high, then usually pitting of the surface takes place. In most cases it is found desirable to employ agitation of the electrolyte, as this largely avoids the production of waves in the finished surface. The agitation is best effected by moving the specimen but other methods of stirring the solution may be employed.

With regard to the time of anodic polishing--this varies very largely with the fineness of the grinding scratches which are initially present on the surface of the specimen. As might be expected, the finer the scratches, the less time is necessary to produce the desired degree of polish. Although the cell arrangement shown in Fig. 56 is typical, alternative types of cell have been proposed; in some of these, the specimen to be electro-polished is actually inserted as part of the wall of the cell, thus, entirely obviating such difficulties as occur in the jigging of the specimen and its electrical contact with the anode. (Fig. 63.)

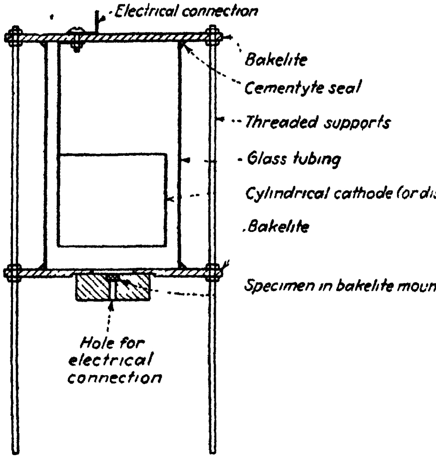

Fig. 63.—Cell used at Bureau of Standards to permit quick removal of specimens from the electrolyte.

ADVANTAGES OVER MECHANICAL POLISHING

The technique described above may be said to be thoroughly established, and is finding increasing use in laboratories which previously employed mechanical polishing methods. It has been found that once a technique for a given steel is established, it may be very readily carried out, and not only is it considerably easier than the corresponding mechanical polishing operations, but also the results are definitely more satisfactory from the metallurgical point of view. For example, one of the big drawbacks to mechanical polishing is the fact that the surface becomes distorted as a result of stress which is set up in the surface crystals, through the mechanical work carried out on the polished surface. This is entirely obviated when electrolytic methods are adopted. Again, all constituents of the material examined remain on the same macrographic level, whereas mechanical polishing may badly affect the softer constituents which may be present.

Another advantage which the electrolytic method possesses is the fact that the time of the polishing process is independent of the size of the specimen to be polished. In mechanical polishing, on the other hand, it is found that the time rapidly increases with the area of the specimen to be polished.

Other electrolytes have been proposed based on phosphoric acid. For example, T. W. Lippert(4) suggested an aqueous solution of orthophosphoric acid of a density of 1·316 for the treatment of a pure electrolytic iron surface. A current density of the order of 30 amp./sq. ft. was employed, a comparatively low voltage (less than one volt) being necessary for an anode area of 0·3 sq. cm. The cathode material was also electrolytic iron. The author reports that the current density value was very critical.

A similar composition was also employed by W. C. Elmore,(5) but the details given are not very explicit.

WORK ON INDUSTRIAL APPLICATIONS

Apart from the reasons already advanced for the difficulty of translating the methods described above into industrial practice, Jacquet, in one of his later publications, crystallises the problem accurately as follows.(6) He says: "It is essential in the first place to point out that those electrolytes which give excellent results in polishing small samples cannot be applied in the industrial polishing of the same metals and alloys." The latter polishing refers, of course, to electrolytic polishing. As his reason, Jacquet points out that high voltages and heavy current densities, which are quite feasible in the laboratory, would not be practicable in the workshop. Furthermore, it had been found necessary in the treatment of different metals to withdraw the samples very rapidly from the bath, washing them very rapidly thereafter, and this again would be difficult to achieve with components of large size. Finally, Jacquet admits that the perchloric-acetic acid type of electrolyte is not a very desirable one to operate in a shop, particularly in view of the gases which are released in the process and which would certainly have to be exhausted in the same manner that the chromium operating solution is dealt with; while also, the mixture is known not to be free from explosive risks.

It is, therefore, to other electrolytes that we must look for industrial application; some of these have already been explored and show considerable promise. It should be noted that very considerable benefit may arise even though the full degree of polish which is desirable is not entirely attained; even a partial polishing effect may help very appreciably to reduce total polishing costs. Progress in this field, therefore, may be expected in gradual stages, whereby the processes initially employed are adequate to produce a certain degree of polish, and may later be replaced by improved processes, in which the degree of polish is increased.

APPLICATIONS OTHER THAN COMPLETE POLISHING

Meantime, there are a number of mechanical processes akin to polishing which are very widely used in the production of steel components and which constitute a further important field for electrolytic polishing technique; some of these are indicated below.

(1) *De-burring.*—Operations such as grinding, stamping, blanking, sawing, etc., often result in the burring of components at this stage in the series of operations. The burrs of course occur at the edges, and since these parts of the article normally receive the highest current density when electrolytically treated, the chances of achieving de-burring by this means are particularly good. It will be appreciated that the electrolytic method is especially valuable where the burrs are not on the external edges of the component, but are situated at points which are normally difficult to reach mechanically, *e.g.*, where the component has received internal blanking or piercing.

J. S. Crout(7) states that the success of de-burring operation is largely dependent on the size of the burrs. Small burrs may be readily dealt with and result in the edges being smoothed, but in the case of large burrs it may involve rather heavy loss of metal from other parts of the surface, and where tolerance limits are imposed the method may not be permissible. As against this, it may be possible to employ stop-offs on the areas where no change in dimension is desired, and usually the throwing power of the solution has been such that it has been possible to clean the interior threads and female fittings without using any special auxiliary cathodes. Thus far, experimental work has shown that the method is applicable to stamped products, such as knives, forks, spoons, etc.

(2) *Machining.*—There are distinct possibilities that electrolytic polishing may be used as a chemical machine tool. The possibility of so doing is obviously linked up with the uniformity with which it is possible to remove metal from a given area on a component. The electrolytic method will only be economically valuable where mechanical methods of machining are either difficult or expensive. For example, a case has been quoted by Crout where certain steel and brass screws had to be made to tolerances which are not possible in a screw machine. The electropolishing method was found to produce the necessary degree of tolerance. The method is being closely studied in the laboratory of the Battelle Memorial Institute, where successful attempts have been made to improve the micro-inch finish on smooth surfaces; thus, mechanically buffed surfaces carrying a 50 to 60 micro-inch finish have been brought down to 40 to 50 micro-inches, and surfaces with a 5 to 7 micro-inch finish have been reduced to 3 to 4 micro-inches. The success of the application is dependent on the existence of inherent pits and inclusions in the steel which, if present, become exposed by electropolishing and prevent the reduction in the micro-inch finish from being affected. The desirability of obtaining such smoothness on steel surfaces is important in such applications as the reduction of the skin friction of parts through which large volumes of gases move at high velocities.

The possibilities of machining electrolytically have reached the stage where investigation is being made at present into the shaping of gears by this method. Obviously, here, a great deal depends on the degree of control which may be imposed in order that metal may be removed sufficiently rapidly from pre-determined sites. This application opens up a wide vista, in that eventually it may be possible to shape and finish a given article in one operation, producing a high degree of finish, freedom from burrs, and at the same time leaving the surface in a non-work-hardened state.

(3) *Increasing adhesion of subsequent deposits.*—With regard to the latter point, namely, the state of surface stress of the component, it is perhaps not sufficiently realised how much stress may in fact be set up through mechanical surface operations. Manual polishing of a metal surface is accompanied by the generation of considerable heat, and as a result the surface stress has a tendency to tear into the macro-structure. It has been shown that the crystal structure of the surface layer may be profoundly affected. Such a surface structure is an unsatisfactory one on which to build an electrodeposit, and normally it is necessary to remove the first crystal layers by etching or similar treatment, before a deposit can be safely applied which will attain the necessary degree of adhesion. As against this, the electrolytically polished metal has been found to be quite free from surface stress, the structure of the surface being similar to that of the body of the metal.

C. L. Faust(8) instances a test which he carried out on nickel-plated steel. In one case, where the surface had been machined and then plated, an Ollard tensile test resulted in the specimen breaking at the interface on the application of 35,000 lb. per sq. in. Thus, the bond of nickel to steel was only of this order, despite the fact that the steel had a strength of approximately 100,900 lb. per sq. in., and micro examination revealed that the failure took place at what was obviously a weak layer of the steel surface. When however, this layer (produced by machining) was removed by electropolishing, and the same section was again nickel-plated, the tensile strength of the bond rose to 90,000 lb. per sq. in.

(4) *Improved protection.*—There is increasing evidence that the electrolytic polishing operation results in a surface effect which secures better protection from corrosion than the same surface after mechanical polishing. Certainly in the case of the stainless steels, it has been found that electropolished components stand up better atmospherically than those which have been polished by abrasive. It is not clear what this is due to, although Faust suggests that it might result from the production of a heavier, denser, more resistant or more uniform covering film, but states, too, that although brass, copper, steel and nickel do not form such a protective film,

electrolytic polishing does, nevertheless, retard the rate of ultimate tarnishing

The difference is strikingly brought out in the reproduction of a photograph published in the *Iron Age*, in 1940(⁹) (Fig 64) The picture shows two samples of identical quality 18—8 stainless steel which were simultaneously exposed for 55 days to the atmosphere of an analytical laboratory fume cupboard Sample A had been electrolytically polished, whereas sample B had received a No 8 mill finish The extreme top of the electropolished sample was untreated, and the top portion of both was lacquered in order to preserve the original finish.

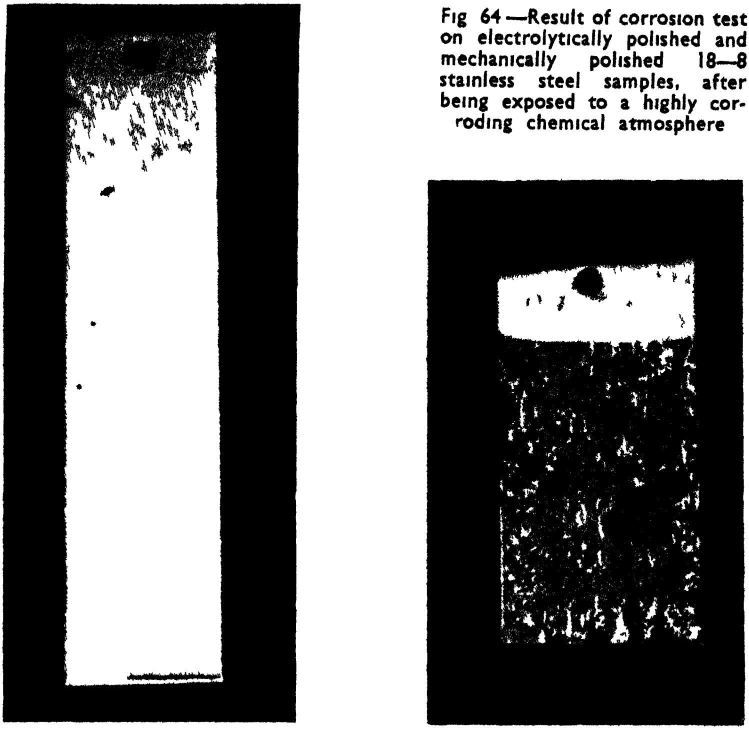

Fig 64.—Result of corrosion test on electrolytically polished and mechanically polished 18—8 stainless steel samples, after being exposed to a highly corroding chemical atmosphere

ELECTRO POLISHED

No 8 MILL FINISH

Another interesting test carried out in a series of tests described by H. Pray and C. L. Faust, of the Battelle Memorial Institute, in the same article, demonstrates the existence of an invisible film on the surface of the electropolished sample. Figs. 65 and 66 show mechanical and electropolished 18/8 stainless steel samples respectively, after they had been subjected to identical etching treatment. It will be seen that in Fig. 66, pinholes have appeared on the electropolished sample, showing the location of attack by the etching material at weak spots in the film

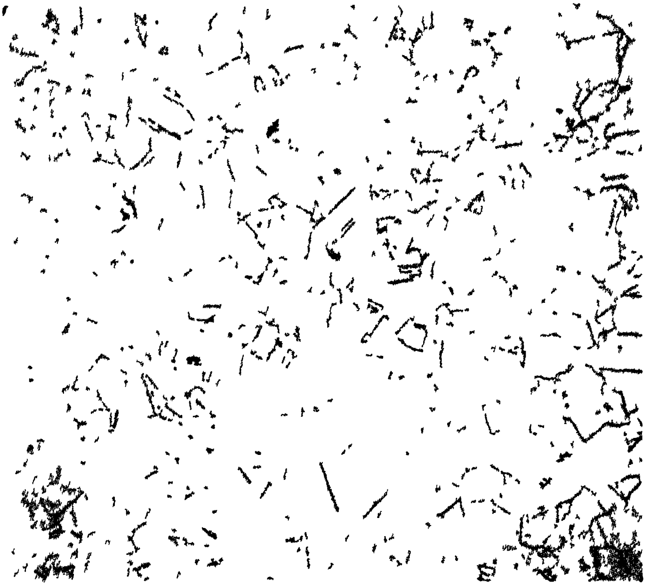

Fig. 65.—Mechanically polished 18—8 stainless steel after subjection to etching (×100)

(5) *Inaccessible polishing.*—Electrolytic polishing obviously comes into its own very definitely where components have to be polished which are of such shape that it is difficult to reach them manually, or mechanically by polishing wheel. Where there are deep recesses, depressions, angles, or cavities, the normal polishing operation is rendered correspondingly more difficult. Fortunately, electrolytic polishing solutions have reasonably high throwing power, and most irregular shapes can be reached by the solution without any special cathodes. Where, however, these are very deeply recessed, auxiliary cathodes have been successfully employed. Among articles

which have been so treated, Crout lists the following: gears, drills, tubing, etc. Where a relief design has been applied to a metal surface, as on tableware, decorative mouldings and jewellery parts, the effect of electrolytic polishing is particularly striking, bringing up the finish very attractively in relief, a result normally very difficult to produce by any other method of polishing.

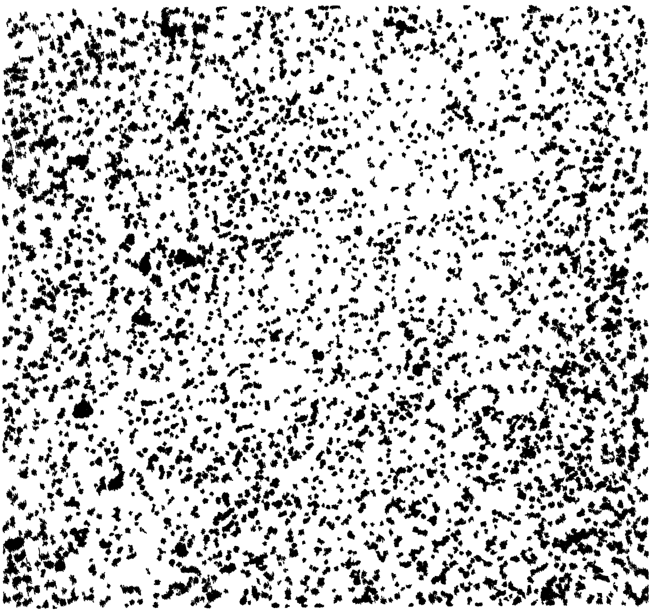

Fig 66.—Electrolytically polished 18—8 stainless steel after subjection to etching (×100)

Crout instances a kitchen utensil which had a semi-spherical shape and was of a size which makes wheel polishing and buffing impracticable on the interior. The hand machine method used for this work did not produce a satisfactory finish. " It was found that an almost mirror-like surface could be produced on both the exterior and the interior by electropolishing, but the amount of metal which had to be removed was excessive. By trial and error, it was found that electropolishing could be used as an initial operation to bring the surfaces to a bright finish, but mechanical buffing would be employed as the final step. This combination of electropolishing and mechanical polishing produced an improved finish and cut out about 80 per cent. of the mechanical polishing previously required."

(6) *Descaling.*—The removal of scale, by electropolishing methods, may also prove in some instances to be attractive. One of the Battelle processes has been applied to parts made of silicon steel which require a smooth bright finish. In this case it was found found that a two-step electropolishing process, using two different solutions, resulted in very satisfactory descaling and brightening. Obviously, however, it is more economic if both these processes can be carried out in a single electrolyte, and it is claimed that this has already been achieved in the case of certain stainless steel aircraft components which carried a heavy scale. Here again, therefore, there are specialised possibilities in the electrolytic polishing field.

COMMERCIAL ELECTROLYTIC POLISHING PROCESSES

Successful application of electrolytic polishing to carbon steels has, up to the present, been largely confined to sulphuric-phosphoric acid processes.

The two main requirements for such a process are: a flexible electrolyte capable of giving reasonably well-finished surfaces on steels of various compositions and surface structures, and one that must at the same time be economical in operation. While certain electrolytes have given satisfactory polishing results, they have suffered from serious disadvantages, *e.g.*, those producing the best polishing results have been found to be either costly and dangerous in commercial use, like Jacquet's perchloric acid-acetic anhydride process, or to possess too short a " life," like the processes using chromic acid, which, while capable of giving mirror finishes when new, deteriorate rapidly due to build-up of reaction products and must be renewed frequently.

A cardinal point is that it is those solutions which tend towards " infinite " rather than " finite " life which are most likely to be economically justifiable. It is thus a primary aim of research in this field to discover solutions in which harmful reaction products are either precipitated, or plated out, and the solutions maintained indefinitely by straightforward additions of their components. The progress in this direction has largely been made in the sulphuric-phosphoric acid type of electrolyte, using various addition agents.

One of the first solutions of this type was evolved by C. L. Faust(10), and contains sulphuric and phosphoric acid in a range of proportions, the optimum being:—

Sulphuric acid	40% (by weight)
Phosphoric acid	49·5%
Water	10·5%

This solution, mentioned among others for various types of steels, has been used for low alloy and plain carbon steels, though as Faust points out, the bath itself and the operating conditions are elastic and must be more or less "tailor-made" to the particular job envisaged.

Normally, however, such a bath is operated at high current density (up to 500 amps./sq. ft.) and at temperatures varying from 100°F.–190°F. Agitation may be employed comprising either work-rod movement or the use of varying degrees of air agitation.

While the total mineral acid content of the solution may thus be up to 90 per cent. by weight, much depends on the amount of water present. In the absence of water, a solution may be used containing as little as 1 per cent. of mineral acid. For instance, another solution by Faust(11) contains:

Glycerol	94% (by weight)
Sulphuric acid	1%
Ammonium chloride	5%

Such solutions, however, are highly viscous, of low conductivity, and slow in action.

An earlier bath referred to by Faust(12) is based on a mixture of sulphuric and arsenic acids. This is applicable not only to plain steels but to the austenitic type of steel, as well as to nickel and nickel alloys, copper and brass. The operating conditions are similar to the sulphuric-phosphoric acid bath, although in this case agitation is considered to be essential. A drawback to this process is that arsenic is plated out cathodically in use, and this appears as flakes floating on the surface of the electrolyte, though, depending on the operating conditions, there is a tendency for it to be redissolved by reaction with As_2O_5 which converts it to the slightly soluble As_2O_3.

Two further types of bath referred to by Faust(13, 14) contain phosphoric and chromic acid, with or without sulphuric acid. An example of the former type contains:—

Sulphuric acid	15% (by weight)
Phosphoric acid	63%
Chromic acid	10%
Water	12%

while a solution without sulphuric acid contains:—

Phosphoric acid	45–88% (by weight)
Chromic acid	0·1–29%
Water	14–37%

the concentration of the components being interdependent and delineated by Faust graphically in a triaxial diagram.

While the operating conditions for the phosphoric-sulphuric-chromic acid electrolyte are on the whole less intense than those for plain phosphoric-sulphuric acid solution (current densities of 200–300 amps./sq. ft. being used), the solutions containing no sulphuric acid tend to require high current densities (up to 1,000 amps./sq. ft.) with temperatures up to 275°F.

As already mentioned, the latter type of electrolytes containing chromic acid, are capable of giving excellent results, but are of the type possessing a "finite life" due to a building-up of trivalent chromium and ferric iron in operation. The precise way in which this happens will be dealt with later.

Faust gives the following practical notes about the operation of the electrolytic polishing process:

"Rack designs, equipment, ventilation, handling problems, etc., are somewhat analagous to those of chromium plating.

"Since electropolishing has much better throwing power than most acid plating baths, racking problems are not too complicated for plant use. There is a small amount of spray, but the liquor is heavy, so ventilation and/or tank headroom is not as critical as for chromium plating, but is desirable at least in heavy production. Light production can be designed without special close ducts. Customary methods of good plating practice are all that are required. Bath control is principally by hydrometer measurement, since water content is the most critical variable. Acid ratio can be varied within wide limits. Although specific gravity is the nominal factor of control, it is actually bath viscosity which must be watched. This changes with metal content in the finite life baths, but empirically designed control schedules have been worked out. Generators are generally in the 12v. to 15v. class. However, for broadest use, it may be desirable to instal 18v. to 24v. sets. Rectifiers are entirely satisfactory."

Apart from the sulphuric-phosphoric acid type of electrolyte, brief reference may now be made to some further published processes claimed to be applicable to carbon steels.

The first of these is due to the Swedish workers E. Bergman, P. Erikson, G. Frey and G. Hildebrand(15), and is applicable to iron, cobalt, nickel, chromium and their alloys. The solution used by these workers is defined in their patent as containing "ions having a position in the lyotropic series, according to Cooper(16) after the sulphate ion."

An example of such a solution applicable to carbon steels contains equal parts by volume of concentrated hydrochloric acid (density 1·19) and water, and is operated at current densities of 150–400 amps./sq. dm., and temperatures of 10°C.–40°C. Hydrofluoric acid can be used instead of hydrochloric acid, and the results are said to be improved by the addition of 0·2 grams per litre gelatin, sulphonated castor oil, etc., which serve as inhibitors. A superimposed a.c. is also recommended.

The current densities employed corresponding to between 1,200 to 3,500 amps./sq. ft. are, however, extremely high, and it is doubtful whether their use in a commercial process could be economically justified for most common applications.

Another process is due to R. P. Delaplace and C. L. Béchard(17) who polished steels in 400 grams per litre phosphoric acid in a non-aqueous solvent such as ethyl alcohol, at 20°C. and 30 amps./sq. dm. It would appear that such a process would require extreme care—efficient facilities for cooling the solution, for example, would have to be available. The authors applied their process to polishing roller bearings.

A more recent process uses an electrolyte containing:—

Hydrochloric acid (commercial) ...	25%	(by vol.)
Glycerol	75%	„

This is claimed to be applicable to most metals, and in particular, for machining purposes, as the rate of solution of the metal is very slow, uniform, and easily controlled by the operating conditions. It is due to R. W. Edmonson(18) who prescribes current densities of 0·1 amps./sq. in. for iron and steels. The process may take some hours and is therefore probably more suited to its specialised purposes than to routine polishing.

A solution based on the sulphuric-phosphoric acid combination, using lactic acid, is used in a process brought out in 1945 by S. M. Weisberg and I. Levin(19). The optimum solution is described by the authors as containing:—

Lactic acid (100%)	33% (by weight)
Phosphoric acid (85%)	40%
Sulphuric acid (conc.)	13·5%
Water	13·5%

though this may be varied within wide limits.

Current densities of 100 amps./sq. ft. and temperatures of 65°F.–90°F. (i.e., room temperature) are said to be sufficient, though the process is a slow one, taking 1–2 hours. As usual, water content plays an important part, thus, baths containing much water, tending to etch rather than polish, unless a high proportion of phosphoric acid is present.

The bath possesses an "infinite" life, iron dissolved anodically being precipitated as ferrous sulphate, losses in sulphate being made good by routine addition of sulphuric acid.

In their study of electrolytic polishing solutions, F. C. Mathers and R. E. Ricks(20) found three processes suitable for polishing carbon steels: (1) a 40 per cent. (by vol.) solution of phosphoric acid in cyclohexanol at 86°C. and 360 amps./sq. ft.; (2) a sulphuric acid solution containing 30 per cent. glycerol and an equal amount of an equimolecular mixture of glycerol and tartaric acid, at 40°C. and 270 amps./sq. ft.; and (3) a 45 per cent. solution of pyrophosphoric acid in dioxan. A fourth solution applicable to iron as well as steels was a phosphoric acid electrolyte saturated with citric acid. The recommended treatment time is short—5 to 10 minutes.

OPERATING FACTORS IN THE SULPHURIC-PHOSPHORIC ACID PROCESS

Composition of solution.—The total acid concentration of the electrolyte should be between 70 and 90 per cent. Water content is critical, and care must be taken in the quality of chemicals used, i.e., density 1·71 phosphoric, and density 1·80 sulphuric acid are preferred for this purpose. In solutions with large water content, the conductivity is high and the voltage required low, while excess water allows the sulphuric acid to attack and etch the metal surface. The optimum water content is probably between 15–25 per cent.

The function of the phosphoric acid has been described as that of a buffer, inhibiting the attack on the metal by sulphuric acid; it reacts with the dissolved metal to form the anolyte resistance layer responsible for the smoothing effect. Phosphoric acid usually makes up approximately 70 per cent. of the total acid concentration.

As regards the ratios of the components, experimental work thus far has shown that best results are generally obtained with solutions containing approximately:—

Phosphoric acid	60% (by weight)
Sulphuric acid	20%
Water	20%

Current density.—Current densities employed in the sulphuric-phosphoric acid process are usually of the order of 200–500 amps./sq. ft., but depend largely on the composition of the solution, and the other operating conditions. Voltages required for these current densities depend on the conductivity of the solution, i.e., on the concentrations of water and sulphuric acid as against the less ionised phosphoric acid; they usually vary from 8 to 15 volts. As will be seen later, it may be possible to reduce the necessary current densities and hence voltages with the help of addition agents.

The optimum current density for a given set of conditions has been found to be closely connected with the *critical* current density, mentioned earlier, and it is interesting to note, as W. A. Sparks(21) points out, that the point on the voltage/current curve showing the characteristic current dip, represents also the minimum value of anode efficiency. At the current density at which this minimum anode efficiency is obtained, the anode polarisation is highest, and the maximum polish is obtained. Lower current densities tend to yield etched surfaces, while with higher current densities there is a tendency towards pitting, and the rate of dissolution of the metal becomes excessive.

Temperatures.—The optimum temperature must be determined individually. It is usually in the region of 55°C.–75°C.

Operating times.—These depend primarily on the initial state of the surface, and the desired finish, as well as on the current density, conductivity of the solution, etc.

Results obtained in working on sulphuric-phosphoric acid solutions, by C. B. F. Young and W. L. Brytcuk(22), showed that a maximum reflectivity was obtained in a certain time, after which it decreased, showing that control of the time on production is important for the production of good finishes. These workers used a photoelectric photometer designed by Prof. Hardy* to measure reflectivity, expressing their results in percentage reflectivity as compared with a glass mirror standard. In this connection it is interesting to note that their highest reflectivity value for the solutions they investigated (excepting only Jacquet's perchloric acid-acetic anhydride electrolyte, which gave 40 per cent.), was achieved by the sulphuric-phosphoric acid solution, which produced a surface of 20 per cent. reflectivity.

Operating times in electropolishing steels can vary between a few seconds and several hours, while times of 5 to 40 minutes are normally required in the solutions under discussion.

Agitation.—A certain degree of agitation is advisable to avoid " streaking," which is due to gas bubbles causing corrugation in the anolyte resistance layer. In viscous solutions, it serves also to prevent non-uniformity in composition. It must be pointed out, however, that care must be exercised or with too heavy agitation the anode film may be destroyed and etching occur. A gentle horizontal oscillation of the anode bar is usually sufficient.

Cathodes.—Various cathode materials have been used of which stainless steel is probably the best. The cathode surface area should be between 5 and 10 times that of the anode. Anode-cathode distances may vary, but are usually closer than those employed in plating practice.

STEELS FOR ELECTROPOLISHING.

The chief difficulties connected with the electrolytic polishing of carbon and low alloy steels lies in the great variety of composition of the metal, as well as the greatly varying conditions brought about by various heat-treatments. In addition, it is of the greatest importance that no segregated metallic or non-metallic impurities should be present, which would cause pits when brought to the surface by electropolishing. " Cleanness " tests are often a valu-

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* J. Optical Soc. of America, Vol. 25, 305 (1935).

able guide to the choice of steels, and it is important, when once an electropolishing process has been developed for a particular steel, to permit as little variation as possible in the composition from one batch to another. Nevertheless, electropolishing solutions should be, and often are, sufficiently flexible for small differences in composition to have little or no effect.

The following table of maximum limits of alloying constituents in steels, polished in the sulphuric-phosphoric acid process, is due to Sparks :—

Nickel	3·75%
Molybdenum	0·5%
Chromium	1·4%
Manganese	1·75%
Vanadium	0·3%

Below this range, alloying constituents do not interfere with polishing, except possibly in high-carbon steels which have a high tungsten content.

THE EFFECT OF ADDITION AGENTS

The purpose of addition agents on the sulphuric-phosphoric acid electrolyte is threefold, being designed to improve the polishing action, e.g., by strengthening the anode film, to extend the range of operating conditions in which the maximum polish is obtained, and lastly, to improve the throwing power. The following are some of the addition agents used in various processes :—

Chromic acid.—The behaviour of polishing solutions containing chromic acid has already been described. It is sufficient at this point to indicate the reactions leading to the deterioration of the electrolyte in operation, during which the red colour of the solution turns first to a red-brown, finally to a green colour. This is due to two causes: (1) a progressive reduction of the hexavalent chrome to the trivalent state the effect of which is heightened by the large difference in anode and cathode areas; (2) the re-oxidation of ferrous sulphate, which has been reduced at the cathode, to ferric iron by the hexavalent chrome, with a corresponding production of further trivalent chrome. The ferric iron so formed is then again reduced at the cathode forming more ferrous iron which will in turn reduce more hexavalent chrome.

The reactions are as follows:—

At the anode: $Fe \rightarrow Fe^{+2}$

At the cathode: $Cr^{+6} \rightarrow Cr^{+3}$, $Fe^{+3} \rightarrow Fe^{+2}$

Chemical reaction: $Fe^{+2} + Cr^{+6} \rightarrow Fe^{+3} + Cr^{+3}$

Ferric iron is soluble and accumulates, as does the trivalent chrome, and when the reactions proceed to the point when 2 to 3 per cent. of trivalent chrome is present, the effect is distinctly harmful. In time, therefore, as the content of the two contaminants rises, the bath reaches a point where a good polish is no longer obtainable and the solution has to be discarded. Experiment with porous plates, similar to the devices used in chromium plating, for the re-oxidation of trivalent to hexavalent chrome, have proved unsuccessful.

The short life of the chromic acid solution is a serious disadvantage in its commercial use. Nevertheless, when new, it is probably one of the best solutions available, with respect both to the finish obtained and the comparatively low current densities employed in its use.

Dextrose.—Another addition agent in use for polishing solutions is dextrose, and recent investigations by Sparks have shown it to be very promising. The optimum composition of the solution containing dextrose is in the region of:—

Phosphoric acid	61% (by weight)
Sulphuric acid	26%
Dextrose	3·5%
Water	9·5%

Smaller concentrations of phosphoric acid in such solutions tend to promote pitting.

Sparks states that the addition of dextrose effectively improves the polish, and reduces the employable current density, though not perhaps to the same extent as chromic acid. Current densities of 250 amps./sq. ft. can be used, and pitting at higher current density ranges is reduced. The nature of the addition agent is discussed by Sparks, who found that dextrose carbonised during operation, and when cool, the solution was covered with carbon residue, which was taken up again on reheating. The suggestion is, therefore, that the effect of dextrose is due to a finely divided form of carbon-black. The big advantage of dextrose over chromic acid is that its solutions have an " infinite " life; iron is precipitated as ferrous sulphate and is periodically removed, sulphuric acid being added to make good losses in sulphate.

Glycerine.—Glycerine has been widely used in electropolishing and as already indicated, is often used in large proportions. Its main purpose was thought to be to increase the resistance of the solution, and hence, decrease the currrent density required to obtain polishing. Its main disadvantages are however that it is extremely viscous and somewhat difficult to handle, and tends to char when heated.

Cyclohexanol.—This compound was found by Mathers and Ricks to replace glycerol in electropolishing solutions. It is said to give a slightly better polish, and does not char when heated. Its advantage lies in the fact that it is not soluble in water and therefore not as easy to swill off the work after polishing.

Up to the present little information is available as to the effect of lactic-, tartaric-, hydrochloric-, and hydrofluoric acid, as well as other addition agents, e.g., ammonium chloride, used in various processes. While C. B. F. Young and K. R. Hesse(23) have recently published an account of the effect of fluosulphonic acid in polishing solutions, their results with a 5 per cent. (by volume) of fluosulphonic acid in (d. 1·71) phosphoric acid, have not as yet been very successful. The effective addition agent, in this case, might well be hydrofluoric acid produced by hydrolysis.

$$HSO_3F + H_2O \rightarrow HF + H_2SO_4$$

Organic Addition Agents.—In the paper already referred to, Sparks gives an account of investigation into various organic addition agents to the sulphuric-phosphoric acid bath, the purpose of which was to strengthen the anode film and maintain the minimum anode efficiency over a wider range. The choice here is limited to addition agents of cation activity and various compounds possessing complex amino groupings were tried as well as a number of wetting agents, including Fixanol, oleyol, triethanolamine, Perminal W.A., Teepol X, and β-naphthol, present to the extent of 0·5 per cent. by weight.

The best of these was Teepol X which, at 65°C.–75°C. and 7·2–7·7 volts gave a high degree of polish in 10 minutes. β-naphthol, on the other hand, produced a dead flat, matt finish.

IDEAL ELECTROPOLISHING PROCESS FOR CARBON STEELS

It is apparent from the foregoing that the ideal electropolishing process for carbon steels has yet to be perfected. Technical details of such processes as have been published are sometimes a little obscure and tend possibly to a purposeful vagueness. Perhaps this is not altogether strange, in view of the fact that the field is open to considerable commercial exploitation, and no doubt those working in it are withholding the most important data in order to protect themselves, and probably have one eye on the patent situation that may arise. At any rate, there can be no doubt that much more remains to be elucidated, and while it is difficult to assess the material which is at present being collected and pigeon-holed in laboratories in America and Europe, the likelihood is that the ideal process has yet to be perfected.

In the author's view, an ideal process would entail the satisfaction of the following conditions.

1. The constituents which are employed in the preparation of the electrolyte must be fairly plentiful, and preferably not too expensive.

2. The constituents must be readily controllable. They should be amenable to fairly easy analysis in the laboratory, and also to reasonable control in the shop. For example, physical tests rather than chemical, in order to obtain a rapid assessment of the condition of the solution, are desirable; thus, density or viscosity measurements may find a useful place in such workshop tests.

3. The conditions of operation should not be too difficult. This entails that the voltage required shall not be too high, and the corresponding current density should also not be higher than, say, 200 to 300 amp./sq. ft. The temperature of the electrolyte, again, should not require to be too extreme; all these operating conditions should not be too critical and should allow of a reasonable range of deviation from the specified figures.

4. The products of the electrolytic reaction should not unduly affect the degree of polish which is progressively obtainable from the solution as it ages. Preferably, useless or harmful products of the reaction should be precipitated and thus become readily removable from time to time, or alternatively, electrodeposited,

and thus automatically removed from the sphere of action. Both these methods have been employed in electrolytic polishing processes, the deposition method, notably, by the Battelle process in the electrolytic polishing of nickel.(24)

5. The conditions of handling the materials and also of operating the process should be comfortable to the worker. This does not exclude the possibility that gases may have to be exhausted, because this has been proved to be quite tolerable, notably in chromium-plating practice

6. There should be the minimum tendency to pitting or etching on the part of the electrolyte when the specified conditions are not exactly maintained.

7. Preferably, a process should be adaptable to other auxiliary processes; for example, de-burring or de-scaling.

It will probably be some time before an ideal electrolyte such as that described above will materialise and, no doubt, very useful processes will, in the interim, come to light which do not satisfy all the above conditions but which, nevertheless, are practicable, and give adequate advantages over present mechanical polishing methods.

One thing is certain, that when the problem of producing a practical method of electrolytically polishing carbon steels is adequately solved, it will provide a very valuable contribution to those industries which employ ferrous materials in bulk—a contribution, the measure of which may be not far short of revolutionary in some cases.

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CHAPTER XIII.

The Industrial Applications of Electropolishing to Non-Ferrous Metals

ELECTROLYTIC polishing was first applied to copper as early as 1931, when Matériel Telephonique(3) patented a process in which various electrolytes could be employed, among them the original pechloric acid-acetic acid solution, but also phosphoric acid solutions containing approximately 70 per cent. H_3PO_4 dissolved in either ether or alcohol.

A phosphoric acid electrolyte was also patented by Jacquet,(2) who gave the current densities as between 100 and 1,000 amp./sq. ft., and used temperatures of 60° to 120°F. As will be seen below, later workers found that the best results with a phosphoric acid electrolyte were achieved at low temperatures, i.e., below 70°F.

After this patent, little of importance in the industrial electropolishing of copper was published till 1942, when C. L. Faust brought out the first of a series of patents applied to, or capable of dealing with, this metal. A process(3) consisting of a solution of one or more mineral acids, together with arsenic acid has in part already been described in the previous chapter. While as we have seen, the mineral acid employed for polishing steel was usually sulphuric acid, Faust preferred either chromic or phosphoric acid for use on copper. Two of the solutions contain :—

(1) Arsenic acid	84% (by wt.)	(2) Arsenic acid ...	15%
Chromic acid	10%	Phosphoric acid ...	60%
Water ...	6%	Water	25%

Optimum operating conditions for these solutions are similar, both being worked at around 55°C. The current densities employed were 385 amp./sq. ft. (for 15 minutes) for the chromic acid electrolyte, and 500 amp./sq. ft. (for 23 minutes) for the phosphoric acid solution. The times of treatment recorded depend on operating conditions as well as the initial state of the surface, and serve as approximate rather than definite guides.

A current density of 500 amp./sq. ft., applied for approximately 30 minutes was also used in a solution for polishing brass, containing :—

Arsenic acid	15% (by wt.)
Phosphoric acid	55%
Chromic acid	3%
Water	27%

It should be noted, however, that Faust in a later publication, states that the solutions tend to plate out arsenic in the form of loose floating flakes and for this reason, are inferior to sulphuric-phosphoric acid solutions in production.

The second of Faust's processes(4) is capable of dealing also with nickel, iron, and other metals and alloys, and employs a sulphuric-phosphoric-chromic acid electrolyte, the optimum proportions of which are given as :—

Sulphuric acid	14% (by wt.)
Phosphoric acid	59%
Chromic acid	0·5%
Water	36·5%

while yet another patent(5) describes solutions containing chromic acid, phosphoric acid, and water only. Faust gives the concentration ranges in the following triaxial diagram, in which A B C D encloses the area corresponding to the proportion of the three components with which polishing can be achieved, while the optimum concentrations are found in the area enclosed by E B F E. (Fig. 67).

Operating conditions for this as well as the sulphuric-phosphoric-chromic acid electrolyte, vary within wide limits, depending on the actual composition. Current densities of 100 to 1,000 amp./sq. ft. are employed at bath temperatures of 60° to 170°F., the best results being generally achieved with approximately 500 amp./sq. ft. at 100°F. Time too, is variable, depending on the state of the surface, and the other operating conditions, and polishing at 500 amp./sq. ft. will take between 1½ to 12 minutes.

TRIVALENT ALUMINIUM IN ELECTROPOLISHING(6)

Probably the best of the processes evolved by Faust for polishing copper employs a phosphoric acid solution containing trivalent aluminium and, optionally, trivalent chromium. The process is

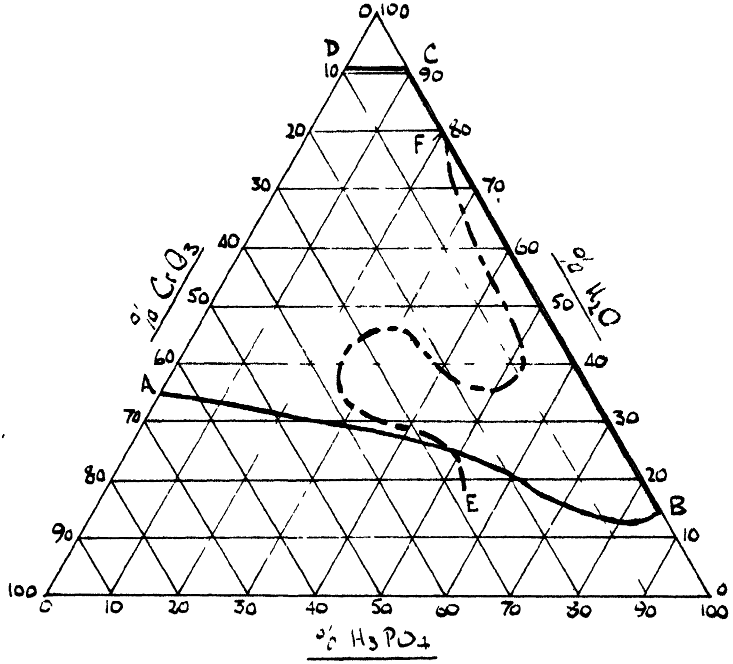

Fig. 67.—Electrolytic Polishing of Copper. The area representing operative compositions is bounded by the solid line A B C D while the optimum compositions are bounded in E B F E

analogous to the one applied to nickel described in an earlier chapter. Baths containing chromic acid deteriorate quickly for reasons already stated : trivalent chromium and, in this case, copper accumulate in the solution and when about 2–3% of the former and 4–5% of the latter are present, the solution is seriously contaminated and must be discarded.

Phosphoric acid by itself, on the other hand, can be used for polishing copper only at impracticably low temperatures, and phosphoric-sulphuric acid electrolytes require high voltages and current densities, without achieving a finish comparable to that obtained in a chromic acid solution.

The new bath, on the other hand, goes some way towards combining the good qualities of the old. Current density ranges are low and not critical, the finish is claimed to be excellent, while the solution is said to have an "infinite life," as any copper in excess of 0·5–1·0% is plated out on the cathode. Further, the absence of sulphuric and chromic acids makes the bath less corrosive and viscous and lead lined equipment can be used with impunity. The process needs little or no agitation.

Composition and Preparation of Solutions.—The composition of the solution may vary within the following ranges:—

Phosphoric acid (H_3PO_4)	75 –84% (by wt.)
Trivalent chromium (Cr^{+3})	0·25– 2·0%
Trivalent aluminium (Al^{+3})	0 – 2·0%
Copper (Cu^{+2})	0·3 – 2·0%
Water (H_2O)	Balance

while Faust obtained his best results with two solutions containing:

	1	2
H_3PO_4 ...	75% (by wt.)	82 % (by wt.)
Cr^{+3}	0·8%	0·5%
Al^{+3}	0·3– 0·6%	0·4%
Cu^{+2}	0·3– 0·5%	0·4%
H_2O	Balance	Balance

There is little difference in operation between the two solutions, though bath (1) has a slightly greater anode efficiency and takes slightly less time.

The solutions may be prepared in two ways. The theoretical amount of metallic aluminium is dissolved in aqueous phosphoric acid by heating. The trivalent chromium salt, preferably chromic chloride, is added, and the solution heated for some time to expel the chlorine, whose presence is injurious to the solution, in the form of hydrochloric acid gas. This is a lengthy operation and should, if possible, be carried out with a small amount of the phosphoric acid in a fume cupboard or under an exhaust. The solution is then made up to the required level with water.

Alternatively, the theoretical amount of chromic acid (CrO_3) is dissolved in the phosphoric acid. The aluminium is added and the solution electrolysed until the chromium has been reduced to the trivalent state.

Operating conditions.—Current densities employed with these solutions may vary from 50 to 250 amp./sq. ft. while those of 100 to 150 amp./sq. ft. normally give the best results. ·Voltages of 4 to 6 are required.

Experiments conducted by Faust showed that the anode efficiency was decreased substantially as current density was increased to the value at which polishing was achieved (approximately 50–100 amp./sq. ft.), after which it remained constant, suggesting that the minimum anode efficiency can, in this solution, be obtained through an extensive range of conditions, and as will be remembered, it is this value, occurring at the critical density, which normally gives the best polishing results.

As current density is increased, so is the range of temperatures at which good polishing is obtained, which with current densities of 100 to 150 amp./sq. ft. may vary between 100° and 130°F.

The anode efficiency is also affected by other factors, and increases with increase in voltage, rise in temperature, and increase in the aluminium content. This suggests that under these conditions more of the basic metal will be dissolved in the process of polishing, and it is probably desirable to keep the temperature and aluminium content as low as good polishing permits.

The use of trivalent chrome in the solution is not essential and good results can be obtained in its absence. In the absence of aluminium, it will however facilitate polishing at high current densities while increasing the voltage and anode efficiency.

Control.—Maintenance of the solution presents no difficulties. Control of acid concentration is by hydrometer, or more accurately by determination of the phosphate content, while chromium, aluminium and copper can be determined by the usual methods. Evaporation losses must be made good by a routine addition of water, and drag-out losses in the other components are replaced from time to time. Copper in excess of 0·5–1·0% of the solution is plated out on the stainless steel cathodes, in the form of copper powder of over 98% purity. This is removed from time to time.

BATTELLE PROCESS FOR ELECTROPOLISHING BRASS

This process,(7) patented by Faust in 1945, is to some extent similar to one of the processes described for polishing copper. It uses a phosphoric-chromic acid electrolyte, whose concentration ranges are shown in the diagram below, in which Faust delineates the working proportions shown in the area A B C D as well as those for optimum polishing enclosed by the broken lines A E L F M G H A and I K J I. (Fig. 68).

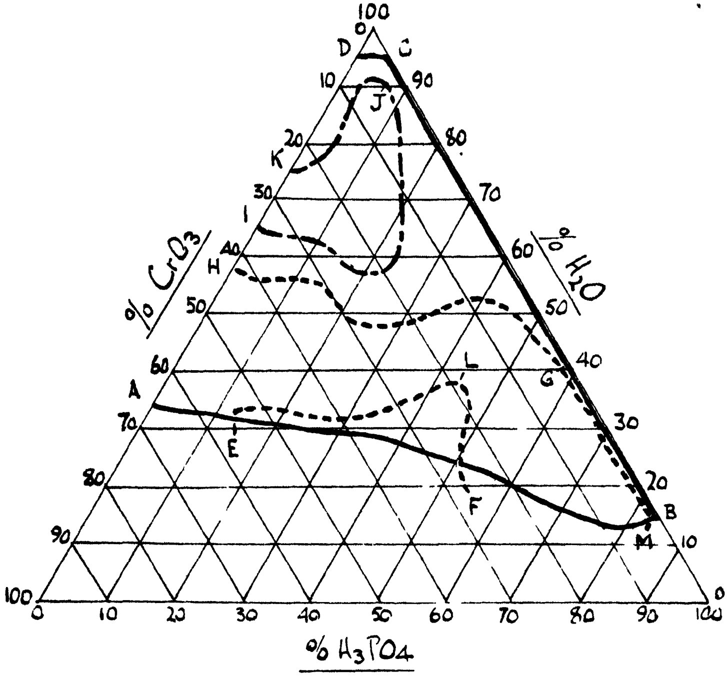

Fig. 68.—Electrolytic Polishing of Brass. Operative composition bounded by A B C D optimum compositions A E L F M G H A and K J I.

Operating conditions vary for the different compositions, but are similar on the whole to those employed in the process for polishing copper.

OTHER PROCESSES.

Some details of at least three further processes capable of polishing non-ferrous metals have been published. The first of these is due to R. W. Edmonson, and employs the same solutions as has already been described for steel, containing 25 per cent. (by volume) of commercial hydrochloric acid in 75 per cent. glycerol. The current densities used for polishing copper are higher than for steel, and are in the region of 36 amp./sq. ft. As will be remembered, this process is an extremely slow one, and its uniform and easily controlled action makes it particularly suitable for use as an electrolytic machine-tool.

J. L. Rodda(8) gives an interesting account of polishing zinc and brass in 200 grams per litre chromic acid in water. The process is, however, of mainly theoretical interest, as current densities in the region of 2,000 amp./sq. ft. are necessary.

The work of Mathers and Ricks has already been referred to. They found copper difficult to polish and their best results were obtained with a 40 per cent. (by volume) phosphoric acid solution in cyclohexanol. A current density of 200 amp./sq. ft. was employed and the bath operated for 5 minutes at 100°C.

Other solutions capable of polishing copper include chromic acid - water, ammonium acetate - glycerine - boric acid, sulphuric acid - phosphoric acid, acetic anhydride - sulphuric acid, and pyrophosphoric acid - cyclohexanol solutions. These electrolytes were found to be very fast in action, most of them requiring polishing times of only 10 to 30 seconds.

The presence of halogen ion, and of excess water, were considered by these authors to be detrimental, tending to cause etching rather than polishing.

COMPLEX ELECTROLYTES FOR ELECTROPOLISHING BRASS

The problem of finding electropolishing processes for brass is, as in the case of carbon steels, complicated by the variety of compositions of the alloy, ranging from gilding metal, of a copper content of 90 per cent., to alloys composed mainly of zinc.

As is to be expected, no electrolyte capable of polishing more than a limited range of copper-zinc alloys has been discovered, and progress made up to the present has been achieved largely with brass in the α-phase, i.e. an alloy of a copper content of 70 per cent. or more. Brass existing in more than one phase, for example 60–40, or $\alpha-\beta$-brass, is difficult to polish, as under conditions in which the α-phase is polished, the β-phase is usually etched.

Two processes using complex electrolytes have been described for polishing α-brass, and in particular the 70–30 alloy known as "yellow brass." They are due to R. W. Manuel(9) and P. Berger.(10)

The first of these is an American process and is also said to be capable of polishing copper and zinc. The solution employed in this process contains :—

Water	100	(parts by weight)
Chromic acid	12·5	„ „
Sodium dichromate ...	37·5	„ „
Acetic acid	12·5	„ „
Sulphuric acid	10·0	„ „

and is worked at 250–1,000 amp./sq. ft. at room temperature, or approximately 86°F. The time for the process varies with the state of the surface, current density, etc. Manuel prefers to use the solution on surfaces on which a preliminary mechanical polishing operation has already been carried out and emery polished surfaces normally require from 2 to 5 minutes, the electropolishing process in this case replacing the final "mopping" and "colouring."

The tank, which can be used as the cathode, is of steel or alloy-steel, though it is preferable to use separate cathodes of the same metal.

The function of the components of the solution are not given in great detail, though Manuel states that the addition of chromate salts appreciably depresses the current density required for polishing, which in a plain chromic acid solution is often as high as 5,000 amp./sq. ft.*

Acetate is stated to function as a buffer, and also to help strengthen the anode film. The purpose of sulphuric acid is to improve the throwing power of the solution as well as to improve the general finish.

A degree of agitation is necessary in the solution and may be accomplished either by anode-bar movement or air agitation. While agitation prevents streaking, it must not be vigorous enough to destroy the anode film. Pitting occurs at times and can be prevented by raising the current density; it is not usually encountered at current densities above 500 amp./sq. ft.

A feature of this solution is its fast rate of polishing, due probably also to a high anode efficiency, which causes a considerable amount of metal to be dissolved. Polishing time is therefore a critical factor and must not be prolonged over the period at which the maximum polish has been achieved.

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* The difference between this figure and that given by Rodda is due probably to difference in composition and operating conditions as well as to the fact that in chromic acid solutions the current density required for polishing increases with time as reduction occurs and trivalent chromium is accumulated.

The second process, due to Berger, has been developed in this country and is in production at a Midland Works, for the purpose of polishing α-brass pressings. It has many features in common with the Manuel process and is used preparatory to bright nickel-chrome plating, the layout of which is shown below. The polishing-plating cycle is continuous, the work being loaded into steel jigs before polishing and unloaded for inspection after chrome plating.

COMPOSITION AND THEORY OF THE BERGER SOLUTION

The development of this process is interesting, and it will be useful to describe briefly the function of the individual components of the electrolyte as envisaged by Berger.

Phosphoric and Chromic Acid.—According to Berger, two types of anode film are formed in electropolishing, both of which will be produced in varying proportions by different electrolytes. In this way the anode film produced in a phosphoric acid electrolyte will be gaseous in character while chromic acid produces liquid films. The two types of film have different properties and while gaseous films afford the greater insulation, hence yield smoother surfaces, and take a longer polishing time, liquid films tend to give rise to undulating surfaces of greater reflectivity, while permitting a more rapid rate of dissolution of the metal.

The solution used by Berger is based on a mixture of phosphoric- and chromic acids and thus affords a compromise between the properties of the two types of film. Good results were obtained with solutions of phosphoric acid : chromic acid ratios greater than 10 : 1 or less than 1·5 : 1 and while the former solution was used with certain brasses containing lead, the latter type was preferred for the plain copper-zinc alloy, as better current distribution and a faster polishing action were obtained.

Sodium dichromate.—The phosphoric-chromic acid electrolyte was found to have poor solvent properties and suffers from rapid reduction of the chromic acid and hence, deterioration. The addition of sodium dichromate to about 10 per cent. from saturation to some extent overcomes these objections, though not entirely, the final solution still having a finite life of some 300,000 ampere hours or, approximately four weeks, for 200 gallons of solution, during

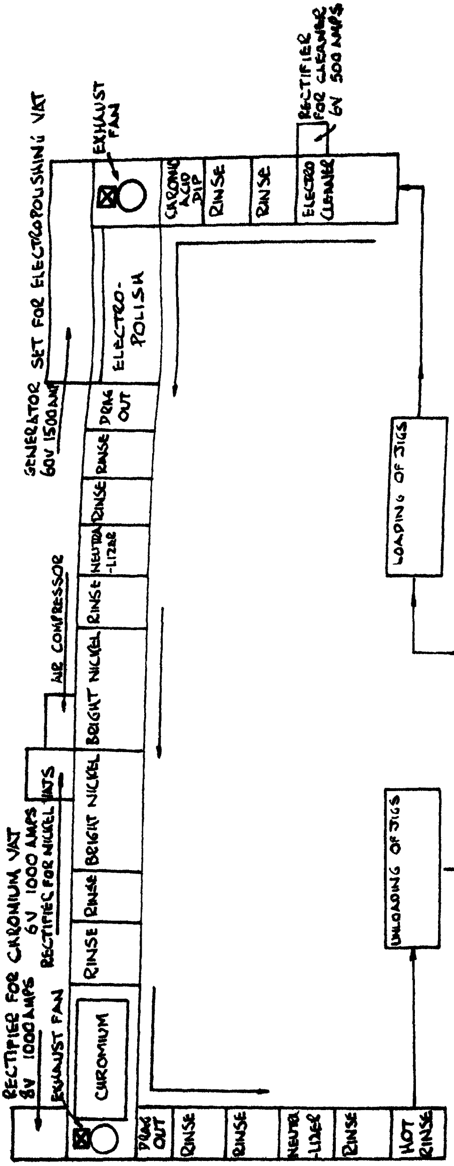

Fig. 69.—A schematic layout of the plant

which the bath voltage increases from approximately 4–6 volts to 14–16 volts.

The way in which the dichromate prolongs the life of the solution is, according to Berger, due to the reduction of both chromic acid and dichromate which retards the total reduction of chromic acid, though he does not make clear what the reactions actually are. As we have seen, deterioration is primarily due to accumulation of trivalent chromium, as well as to the oxidising action of the hexavalent chrome on the solution products (in this case copper) converting it to a soluble form, which may be of assistance in strengthening the anode film, but is detrimental to the solution when present in excess. Both chromic acid and dichromate will be reduced to trivalent chrome, whose concentration should therefore not be affected, while the concentration of chromic acid does not appear to be a major factor since routine addition of this compound has no effect. The function of dichromate may therefore need further elaboration.

Hydrofluoric and Sulphuric Acid. These compounds are designed to improve the current distribution of the electrolyte and overcome a certain "graininess" of the surface. While hydrofluoric and sulphuric acid are now used, the best effect was achieved with sulphamic acid which was not, however, available at the time in sufficient quantity. In this connection it is interesting to remember that Manuel employed sulphuric acid for the same purpose, and it would, further, be interesting to discover to what extent sulphamic acid is actually hydrolysed in this strongly acid solution :—

$$NH_2SO_3H + H_2O \rightleftharpoons H_2SO_4 + NH_3$$

Acetic Acid or Propionic Acid.—The sulphuric acid in the solution tended to reduce the insulation of the anode film, and it was found necessary to counteract this by the addition of a compound with high electrical resistance. Carboxylic acids proved satisfactory for this purpose, the best results being achieved with acetic and propionic acids in concentrations of 90 to 150 grams per litre.

The final solution had the following composition :—

Basic solution :	Phosphoric acid	70– 90% (by wt.)
	Water	10– 30%
Addition agents :	Chromic acid	180 g/l
	Sodium dichromate	420 g/l
	Sulphuric acid	80– 95 g/l
	Hydrofluoric acid	3– 6 g/l
	Propionic or acetic acid	80–150 g/l

OPERATING CONDITIONS

Current densities of 100 to 1,000 amp./sq. ft. may be used, while the best polishing is achieved with 140 to 350 amp./sq. ft. Temperatures of 60° to 120°F. can be employed, and while the best results are usually obtained at 75°F., Berger found that the insulating film broke down above 120°F. Maximum throwing power was obtained by training small cathodes at all angles, between 12 inches to 30 inches from the anode, the total cathode area being roughly equal to that of the anodes.

Electropolishing time for this process varies between 2 to 7 minutes and vigorous air agitation is used to prevent streaking. The amount of metal dissolved under average conditions is of the order of 0·0003 inch per minute.

CONTROL OF THE SOLUTION

Berger gives no descriptions of analysis of the solution and due to the complexity of the electrolyte, this would not be easy. Routine additions of chromic acid, sodium dichromate and sulphuric acid are made according to ampère-hour consumption, while the solution is replaced completely about once a month at a cost of about 3s. 7d. per gallon.

While chemical analysis of the major constituents of the solution would not be impossible, it is probably better in a complex solution of this type to make routine additions where these can be based on experience of the process, drag-out losses, etc., helped by specific gravity measurement, making use of as much chemical analysis as can conveniently be carried out.

CORROSION RESISTANCE OF ELECTROPOLISHED BRASS

Several authors have reported that the corrosion resistance of electropolished brass is superior to that of the mechanically polished metal, reasons for which have already been discussed in an earlier chapter. Nevertheless, neither electrolytically nor mechanically polished brass surfaces will withstand prolonged exposure. By a neutralising dip used after electropolishing, Berger now states that using certain unnamed additions, a transparent anodic film may be produced which is absorbed by the metal and is corrosion resistant. For work which is to be plated, the use of such a dip has a detrimental effect on the adhesion of the deposit.

APPLICATIONS OF ELECTROPOLISHING

In the processes described for non-ferrous, as indeed for most other metals, the results achieved are far from perfect. No entirely satisfactory process has yet been discovered, the two major qualities, a mirror finish and an "infinite" life, having so far proved largely incompatible. Another limitation of present-day processes lies in the polishing action itself. Thus, while it is often possible to impart a mirror-like finish to dull uneven surfaces, it is extremely difficult to remove die marks and deep scratches which may by electropolishing even be accentuated. It may be possible to overcome this in the future, but at present it is usually necessary to employ a rough polishing operation before electropolishing, or alternatively, use only metal which is free from surface scratches and exercise particular care in its handling.

Nevertheless, the progress already made is substantial. Thus, despite the above limitations, electropolishing of brass is already practised commercially on a significant scale—particularly on articles which require a brilliant rather than a polished finish, *e.g.*, costume jewellery, cruet tops, etc. Processes such as those described above have gone a long way towards perfecting a major application of electropolishing, and its possible incorporation into a continuous plating cycle without intermediate mechanical operations.

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APPENDIX

The Development of Bright Nickel Plating in America

WHILE the greater part of bright nickel plants in operation in this country employ electrolytes of the cobalt-nickel type, American practice has largely been concerned with the organic type of solution, whose forerunner, the Schlötter solution(1) has already been described. This Appendix has been added to acquaint readers of the most popular solutions in use in the United States to-day.

Colloid-forming compounds capable of giving bright deposits when added to nickel plating solutions are numerous, though deposits formed in this way tend towards embrittlement. A further disadvantage common to most brighteners is that they are effective only when present in a narrow range of usually very low concentrations, and are thus difficult to control. Most electrolytes of this type, therefore, contain a second, and sometimes a third, addition agent, designed to stabilise the solution, improve the action of the brightener over a wide range of operating conditions and increase the ductility of the deposits. In this way electrodeposits of high lustre and excellent quality are achieved.

Among the processes employed in America, three of the most widely used have been developed by the Harshaw Chemical Company, the McGean Chemical Company and the Udylite Corporation. These processes all use metallic and/or organic brighteners, together with other addition agents, which are usually sulphonates, sulphonamides or other sulphur-containing aryl compounds. It is also usually found desirable to add a wetting agent to the solution. The basic nickel solution may in these processes be either a Watt's solution or a solution based on nickel chloride.

HARSHAW PROCESSES

The series of processes developed by the Harshaw Chemical Company was developed from 1937 onwards, and employ a Watts nickel solution containing:—

Nickel sulphate (hexahydrate)	120–450 g/l
Nickel chloride	15– 75 g/l
Boric acid	15 g/l to saturation

with the addition of two addition agents, which in the case of the first of the processes(2) was selenium or tellurium and one of a group of sulphonates whose function was to retard the deposition of the brightener and to increase the ductility of the nickel. The metal brightener, which could be added in the form of the oxide, one of the oxy-acids or organic compounds of selenium or tellurium, was present in the solution to the extent of 0·005 to 0·05 per cent., and is co-deposited from a solution containing sulphonate to the extent of approximately 0·3–0·5 per cent.

The sulphonate addition agent is taken from a group of compounds including α- and β-naphthalene sulphonates, naphthalene di- and trisulphonates, diphenyl sulphonates, and the reaction products of sulphuric acid on naphthalene derivatives. This addition agent may be present to the extent of 0·05 to 1·0 per cent. of the solution.

The solution is worked at a low *p*H (*p*H 3·0–4·0), and pitting is prevented by the addition of a wetting agent in sufficient quantity to reduce the surface tension of the solution to below 40–50 dynes/cm. The wetting agent employed is normally lauryl alcohol sulphate or some other sulphonated aliphatic alcohol containing 8 to 20 carbon atoms.

Current densities of 10 to 100 amps./sq. ft. may be employed, and the optimum bath temperature is approximately 50°C. An example of this type of solution contains:—

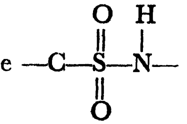
Nickel sulphate (hexahydrate)	26 oz./gall.
Nickel chloride	4 ,,
Boric acid	4 ,,
Selenium oxide	0·01 ,,
Naphthalene disulphonic acid	1 ,,
Lauryl alcohol sulphate	0·01 ,,

Selenium and tellurium containing solutions have, however, a tendency to produce a film on the deposit, which must be removed prior to chromium plating. This can be achieved(3) by anodic-cathodic treatment in an 8 oz./gall. sodium cyanide solution, in which part of the cyanide may be replaced by carbonate or formate. The work is made anode for a few seconds to remove the film, then the current is reversed for up to half a minute which "reactivates" the nickel surface.

Later processes of the Harshaw Chemical Company(⁴) employ the same basic nickel solution as above, but use organic brighteners as well as one or more addition agents of a group of sulphonates, sulphonamides and sulphimides, and a wetting agent. The second addition agent is the same in all the processes and is taken from the following group:

α-Naphthalene sulphonate,
β-Naphthalene sulphonate,
Naphthalene disulphonate,
Naphthalene trisulphonate,
o-Benzoic sulphimide.

Benzene sulphonamide
Benzene sulphohydroxamic acid
p-Toluene sulphonamide
o-Toluene sulphonamide

These compounds have the  $-\mathrm{C}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{\mathrm{S}}}-\overset{\overset{\displaystyle H}{|}}{\mathrm{N}}-$ group in common and can be used in a wide range of concentrations, i.e., from 1 g/l to saturation; 5 g/l being normally employed. The compounds are frequently used in the form of their salts, one of the most commonly employed, for instance, being o-benzoic sulphimide (saccharine) of which the sodium salt is normally used.

A wetting agent is recommended in all cases to avoid pitting. Sodium lauryl sulphate is commonly used, in the form of "Duponol M.E. dry" while two other proprietary compounds "Tergitol 4" and "Tergitol 08" may also be employed.

BRIGHTENERS

Numerous brighteners are mentioned in the patent, falling into several distinct classes of compounds. The amount in which they are present in a plating solution varies usually between 0·001–0·1 g/l depending on their embrittling effect on the deposit and often their solubility. Inorganic or organic salts are frequently preferable to the original compound as these have higher solubilities, chlorides, hydrochlorides, sulphates and acetates being the salts most commonly employed. The brighteners mentioned are too numerous to list in the space available, and as it is often not indicated which of them give the best results, it will suffice to list the classes of compounds from which they are selected, giving one or two examples, together with their optimum concentration ranges. Compounds recommended as the best of their classes are underlined.

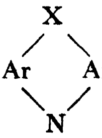
(A) DYES AND DYESTUFFS

(1) Azo compounds of general formula Ar N : N Ar′. The aryl groups (Ar and Ar′) are preferably benzene nuclei carrying 1–3 amino substituent groups, e.g., *Chrysoidine* ($Ph-N{=}N-C_6H_3(NH_2)_2.HCl$) 0·010 g/l. *p-amino azobenzene, triamino azobenzene*, 0·015 g/l., etc.

(2) Stilbene dyes, e.g., *Pontamine Yellow SX* (sodium dinitroazodistilbene tetrasulphonate) 0·05–0·25 g/l.

(3) Amino polyaryl methanes : tri- and di-phenyl methane dyes, chieflly fuschsonimonium compounds, e.g., *Fuchsin* p,p′-diamino-m-methyl fuchsonimonium chloride), *reduction—and carbitol—products of fuchsin and a mixture of these,* 0·003–0·030 g/l; etc. 2,2′,4,4′*-tetramino*–5,5′*-dimethyl diphenylmethane sulphate,* 0·010 g/l; etc.

(4) Xanthene Dyes, e.g., *Rhodamine S* (Tetramethyldiaminosuccinyl-xanthylium chloride), 0·25 g/l; etc.

(5) Aromatic Nitrogen compounds of formula 

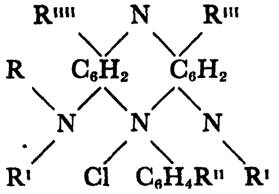
where x=N, C, S, O, or these elements carrying other atoms or groups *ortho* to the aryl nuclei. These are preferably benzene carrying 1–3 amino substituent groups. Among these compounds are :

(*a*) Acridine dyes : where x is a ≡ CH group, e.g., *Rhodamine Orange* 0·025–0·05 g/l; *dimethyldiaminoacridine hydrochloride,* etc.

(*b*) Thiazole dyes : e.g., *Thioflavine TCN,* 0·025–0·125 g/l.

(*c*) Indamine, indoaniline and indophenol dyes, e.g., *Hansa Green G.S.,* 0·025–0·05 g/l. (See also amino aryl amines.)

(*d*) Azine dyes, where x is nitrogen, e.g., *diaminodiphenazine; Safranine Y,* 0·001–0·05 g/l; and including also safranine compounds of formula



where R, R', R'', R''' and R'''' are H, —CH_3 or —C_2H_5

e.g., *ms-phenylditolylazonium chloride; ms-phenyldiaminodiphenyl azonium chloride,* 0·1 g/l; etc.

(*e*) Oxazine dyes: where x is an oxygen atom, e.g., *diaminophenoxazine*: *Basic Navy Blue O,* 0·025–0·050 g/l; etc.

(*f*) Thiazine dyes: containing sulphur, e.g., *Lauth's Violet* (diaminophenazthionium chloride); *Methylene Blue* (tetramethyldiamino-diphenazthionium chloride); 0·025–0·05 g/l; *Toluidine Blue; Thiocarmine R,* etc.

(*g*) Oxyquinone and oxyketo dyes, e.g., *Newport Acid Anthraquinone Blue AR* 0·05–0·25 g/l.

(6) Amino polyaryl amines of general formula Ar NH Ar′, the best of which are the amino substituted diphenylamines, e.g., *2, 4-,* and *4, 4- diaminodiphenylamine,* 0·01–0·02 g/l; *4- aminodiphenylamine,* etc., *Phenylene Blue; Indophenol; 2, 2′, 4, 4′, 6, 6′ – hexaminodiphenylamine,* 0·01–0·017 g/l; etc.

(7) Allied aryl Compounds, such as *benzidine acetate,* 0·004–0·010 g/l; 2, 4- *diaminophenol hydrochloride,* 0·005–0·010 g/l; *m-toluylenediamine,* 0·05 g/l; *Phenylenediamine sulphate,* 0·004–0·010 g/l; *phenylhydrazine,* 0·02 g/l; *pyrrhol,* 0·05–0·10 g/l; *aminoazobenzene sulphonic acid,* 0·005–0·010 g/l; *picramic acid* 0·005–0·010 g/l; *p-nitroaniline,* 0·004–0·008 g/l.

(B) ALKALOIDS

Quinine bisulphate, 0·008–0·020 g/l; *nicotine sulphate,* 0·004–0·010 g/l, also salts of *cinchonine* (0·005–0·010 g/l), *theobromine; caffeine; apomorphine; atropine; papaverine; ephedrine; morphine; brucine;* etc.

The operating conditions of solutions of this type may vary slightly with the type of brightener and sulphonate employed, but *are on the whole similar to those of the selenium or tellurium* process.

PROCESS OF THE MCGEAN CHEMICAL COMPANY

This process, covered by two patents(⁵) employs a nickel solution containing:

Nickel sulphate	180–360 g/l
Nickel chloride	8–75 „
Boric acid (or nickel acetate)	8– 45 „

as well as two addition agents: (1) a sulphonate of a naphthalene or toluene derivative, and (2) a soluble salt of either zinc or cadmium. The first of the addition agents is taken from a group consisting of sulphonic acids of naphthalene, naphthol, naphthylamine, toluidine and tolidine, and may be present in the solution to the extent of 1 g/l. to saturation, which is often the limiting concentration.

The function of the sulphonate is said to be that of "promoter" or "catalyst" in the production of bright deposits and results are said to be improved when they are mildly chlorinated, e.g., by the action of chlorine water. They may also be used in the form of their sodium salt.

Zinc or cadmium are usually added as the sulphate, chloride or sulphonate and, in the presence of naphthalene sulphonates, are employed in amounts of up to 1·6 g/l. zinc or 2·3 g/l. cadmium sulphate, the solution being slightly less than decinormal with respect to these metals. When toluidine sulphonic acids are used, the metal brightener is used in smaller amounts, i.e., up to 0·2 g/l. cadmium, or 1·0 g/l. zinc.

Two examples of solutions may be given, containing:

	(1)	(2)
Nickel sulphate	293 g/l	320 g/l
Nickel chloride	12 g/l	12 g/l
Boric acid	—	31 g/l
Nickel acetate	25·5 g/l	—
β-Naphthalene sulphonic acid	2 g/l	2 g/l
Zinc sulphate	decinormal	—
Cadmium sulphate	—	decinormal
*p*H	3·7	2·6

Toluidine sulphonic acids are used in greater concentration than naphthalene derivatives; p-toluidine sulphonic acid, for instance, is often used in concentrations of up to 24 g/l.

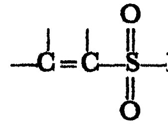
Operating Conditions.—These nickel solutions are worked at between *p*H 2·2–4·25, depending on the composition, and addition agents used; bath temperatures should be between 40–60°C., preferably around 50°C., while current densities of between 25–70 amps./sq. ft. may be employed. The deposits are claimed to be ductile and often contain up to 4·3 per cent. zinc or 0·8 per cent. cadmium as well as approximately 0·08 per cent. carbon and 0·04 per cent. sulphur.

PROCESSES OF THE UDYLITE CORPORATION[6]

Three processes have been developed by the Udylite Corporation, all of which employ sulphonates or sulphonamides as an addition agent, using in addition either: zinc or cadmium, ketones or aldehydes or their halogenation products, or soluble salts of thallium.

The basic electrolyte may be either a Watts or Chloride type of nickel solution, and is buffered with boric- or formic acid. Sodium and ammonium salts are, however, undesirable, especially in the presence of zinc or cadmium, while acetate and citrate should also be absent.

In the first process, the following sulphonamides or sulphonimides may be used: *Benzene sulphonamide,* 1–3 g/l; *o-Benzoic sulphonimide* (saccharine), 1–2 g/l; *β-naphthalene sulphonamide,* 0·5 g/l; *p-benzoic sulphonamide* 0·5–1 g/l, *o-* or *p-sulphondichloramide* 0·5–1·0 g/l; *o-, m-* or *p-toluene sulphonamide* 1 g/l—saturation; etc. The upper limit of the concentrations of these compounds is usually imposed by the saturation point, and the more soluble compounds, e.g., benzene sulphonamide, toluene sulphonamide and saccharine are usually preferable.

The concentration of these addition agents affects the bright current density range, which in the case of the less soluble compounds is usually low. The strength of the bond between the sulphur and carbon atoms in the  $-\overset{|}{C}=\overset{|}{C}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-N=$ group also plays a part. Due to its different orientation, for instance, α-naphthalene sulphonamide gives superior brightness over a wider range of current densities than the β-compound. An odour of naphthalene is distinguishable at the cathode in the use of the former. The β-compound appears to be more stable and in operation gives on the whole better results than its isomer.

The best results are obtained when 0·3 g/l zinc or 0·4 g/l cadmium are used together with 1–3 g/l benzene or p-toluene sulphonamide or a mixture of two soluble sulphonamides. The bath temperature may be between 100°–160°F., and the solution operated at between *p*H 2·5–4·5, the lower *p*H values being used with lower temperatures.

The second of the processes employs a solution containing 75 g/l nickel, 15 g/l chloride (as Cl^-) and 35 g/l boric acid, as well as a ketone or aldehyde of formula R_1—CO—R_2 which as well as being a brightener is claimed to suppress pitting. Phenyl sulphonic acids and soluble indigoid dyes containing the chromophoric group $(O{=}\overset{|}{C}{-}\overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}{=}O)$ are also used in these solutions.

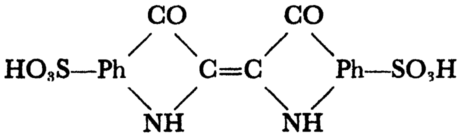
As well as aldehydes and ketones of the types described, halogenated aldehydes may be employed, and more particularly those where the halogen is linked to the α-carbon atom. The latter are said to be more stable and do not tend to resinify in the plating solution. The following are among those listed: *Furfural* (0·1–0·2 g/l), *crotonaldehyde* (0·1–0·2 g/l), *butyl chloral hydrate* (0·2–1 g/l), *bromal* (0·2–1·5 g/l),, *diacetyl* (2 g/l), *acetyl acetone* (2 g/l), etc., while the best of the halogenated aldehydes are: *α-brom β-chlor crotonaldehyde* (0·1–0·2 g/l) *α chlor β-chlor crotonaldehyde* (0·1–0·2 g/l) and *α, α-dibrom β-mono chlor butyraldehyde* (0·1–0·5 g/l).

Polymerised aldehydes such as paraldol may also be used, and they have the same effect as the simple compound. The optimum concentration of the carbonyl compounds tends to decrease with increase in temperature, degree of agitation and increase in *p*H of the solution, as well as with decrease in the nickel concentration.

Mixtures of two or more aldehydes often widen the plating range and mixtures commonly used include 0·3 g/l *bromal hydrate* and 1 g/l *butyl chloral hydrate;* 0·5 g/l *chloral hydrate* and 0·4 g/l *dibromo–chlor–butyraldehyde hydrate;* or 1 g/l *butychloral* *hydrate* and 2 ml/l *formaldehyde* (40 per cent.), etc.

The concentration of the aldehydes usually reaches an optimum point, and though formaldehyde, for example, may be used in amounts up to 6 g/l, the results are no better than those achieved with 0·75 g/l. Halogenated aldehydes, however, have an adverse effect on the adhesion of the deposit, if present in too high a concentration.

The other addition agent may be of two kinds : (*a*) an aromatic sulphonic acid (which must not contain the amino groups uncombined with an acid group or unprotected phenolic groups), and (*b*) a soluble indigoid dye containing the chlormorphic group. Examples of compounds used for this purpose are :(*a*) *dichlorobenzene sulphonic acid* (3 g/l); *o-chlor p-toluene sulphonic acid* (5 gl); *p-bromobenzene sulphonic acid* (4 g/l); *o-benzaldehyde sulphonic acid* (4 g/l), *coumarin sulphonic acid* (2 g/l), *toluene sulphonamide* (4 g/l), etc., *naphthalene mono-, di-, or tri-sulphonic acid* (2–5 g/l), *propyl-, butyl-, cyclohexyl- or benzyl-naphthalene sulphonic acid* (1–3 g/l) may also be used. Class (*b*) contains *Indigo carmine*,



(3–7 g/l); *Ciba Blue 2B* (2–5 g/l) and *Ciba Green* (disulphonic acids) (1–4 g/l).

The concentration of the sulphonatic addition agent is on the whole not critical. The solutions are normally worked at approximately 50°C., and at between *p*H 2–5·5, while current densities of 1–5 amps./sq. dm. may be employed. The throwing power of the solution is said to be good and is improved with the use of lower temperatures and higher *p*H's, the optimum *p*H value lying usually between *p*H 4–5·3 (electrometric).

The third of the Udylite processes employs thallium, as well as an aryl sulphonamide, sulphonate or sulphinate, containing the $=C-\overset{+}{SO}-$linkage. The latter compound may be either *o-benzoic sulphimide* (saccharine) (1–3 g/l); *benzene mono-* or *disulphonamide* (1–3 g/l and 0·25–1·0 g/l), or *o-* or *p-toluene sulphonamide* (1–2 (2·5) g/l); and may be added to nickel plating solutions of one of three types, containing :

	(1)	(2)	(3))
Nickel chloride...	250 –300 g/l	200 –250 g/l	—
Nickel sulphate...	35 – 45 g/l	75 –100 g/l	200 –350 g/l
Boric acid ...	35 – 40 g/l	35 – 40 g/l	35 – 40 g/l
Temperature ...	40 – 60°C.	40 – 60°C.	40 – 60°C.
*p*H	2·5– 4·5	2·5– 4·5	2·5– 4·5

The thallium is added to the solution as a thallous salt, the sulphate, chloride, carbonate or hydroxide being employable. Nitrate should be absent.

When used in the absence of sulphonamides, 1 g/l thallous sulphate will give bright deposits at above 30 amps./sq. ft., while low current density areas are dark. With increasing concentrations, the dark plate extends to high current density areas, and while lowering the *p*H will decrease this effect to some extent, the deposit is made brilliant and ductile over a wide current density range by the addition of the second addition agent already described.

The thallium ion acts similarly to the zinc ion in solution, and may to some extent be replaced by it. Its optimum concentration range lies between 0·24–1·6 g/l, and a solution containing, for instance, 1 g/l thallous sulphate, 1·5 g/l saccharine, and 1·5 g/l p-toluene sulphonamide is claimed to produce lustrous, ductile deposits at current densities above 3 amps./sq. ft.

The precise way in which the second addition agent operates is not known, but the authors of the process advance the theory that the process involving reduction and hydrogenolysis of the sulphur in the $=\mathrm{C}\text{—}\overset{+}{\mathrm{S}}\mathrm{O}\text{—}$ group, produces an inhibitor in the reduction of the thallous ion. The bath is therefore made more tolerant to these substances as they are less easily reduced in the presence of the $=\mathrm{C}\text{—}\overset{+}{\mathrm{S}}\mathrm{O}\text{—}$ compounds. The degree of effectiveness of various compounds of the class would seem to depend on the precise inhibitor formed, and while the aryl sulphonic acids are more easily reduced than sulphonates or sulphonamide, they form more inhibitor, making possible greater concentrations of thallium. They do not, however, produce the highest degree of brightening as do aryl sulphonamides.

Wetting, or emulsifying agents may be used in all the Udylite processes and are frequently alkyl alcohol sulphates containing 6–8 carbon atoms; butyl-, hextyl, or naphthalene sulphonic acids may also be used.

PROCESSES OF E. I. DU PONT DE NEMOURS & COMPANY[7]

The first of the processes developed by this Company was patented in 1937 and employs a Watts-type nickel solution containing:

Nickel sulphate	95 g/l
Nickel chloride	15 „
Boric acid	15 „
Ammonium chloride	15 „

as well as a brightener consisting of a reaction product of an aldehyde or ketone with an alkali metal cyanide. The best results are claimed to be achieved with " aldacets," which are aldehydes forming a similar equilibrium mixture in cyanide solution, consisting of acetaldehyde, aldol, crotonaldehyde and paradol. These compounds when added to the solution are converted to some extent to this mixture, either by condensation or polymerisation reactions. Cyclohexanone and certain aromatic aldehydes, in particular benzoin or benzaldehyde, may also be employed.

This brightener is normally used in the solution to the extent of 1–3 g/l, while the optimum *p*H is approximately 5·9.

Another process by this Company employs two addition agents, the first of which is methyl naphthalene sulphonate, and the second, sulphite cellulose waste, and an example of a solution contains:

Nickel sulphate	250 g/l
Nickel chloride	15 „
Boric acid	35 „
Sulphite cellulose waste	2 „
Methyl naphthalene sulphonate ...	1·5 „

The solution is operated at temperatures around 50°C., and is worked at a high *p*H, i.e., between *p*H 5·0–6·0, current densities of 50 amps./sq. ft. are usual, and over 75 amps./sq. ft. may be employed in agitated solutions. The " commercial " quality nickel salt of methyl naphthalene sulphonic acid may be used, which contains both the α- and β-isomers. The sulphate cellulose waste or a derivative: lignin sulphonic acid, is used in concentrations of 1–5 g/l.

The third of the Du Pont de Nemours processes uses a "sulphurised proteinaceous" material as addition agent, and claims to possess a first-rate brightening action on dull surfaces, and excellent throwing power.

The brightener is prepared from gelatin, glue or blood or egg albumin by hydrolysis with the enzyme pancreatin (or trypsin) and calcium hydroxide solution, the hydrolisation product being then sulphurised by treatment with carbon disulphide, and acidified. It is used either in a Watts- or Chloride-type nickel solution, in concentrations of 0·05–5 g/l.

A second addition may be made to the solution to improve the deposit, and this is usually 0·5–15 g/l of either o-, or m-sulphobenzaldehyde, or an aliphatic sulphonic acid with a cyclic substituent, as for instance, 2-phenyl ethylene sulphonic acid, or 2-hydroxy—2-phenyl ethane sulphonic acid. Sulphobenzaldehyde may also be replaced by methyl naphthalene—or isopropyl sulphonic acid, etc. In the presence of the second addition agent, the sulphurised protein material may be present in concentration of as low as 0·005 g/l. An example of a solution employed contains:

Nickel sulphate	350 g/l
Nickel chloride	15 „
Boric acid	35 „
Sulphurised Proteinaceous material ...	0·005–0·5 g/l
o-sulphobenzaldehyde	5 g/l

The last three processes are all worked at comparatively high *p*H values and do not therefore require the use of wetting agents. This, it is said, reduces the risk of contamination from oil, which when present in solutions of low surface tension, is emulsified and dispersed.

OTHER PROCESSES

Several other processes using organic type bright nickel solutions appear in the literature. These are mentioned briefly below.

The first of these, by the Parker Wolverine Company(8) employs the original Schlötter addition agent; nickel benzene disulphonate, together with a soluble zinc salt in a Watts nickel solution. Nickel benzene disulphonate is present to the extent of approximately 11 g/l, and zinc in concentration of 1–3 g/l, in the form of the sulphate.

A British process by G. E. Gardam and H. N. Priston(9) also employs a Watts solution, containing the sodium salt of either benzene-, toluene-, ethyl benzene- or α-naphthalene sulphonic acids, in concentrations varying from 15–30 g/l. The solution also contains 0·02–0·04 g/l of a colloid which may be either gelatin, dextrin or lysalbic acid. It is operated at between 40°–60°C., at current densities of 20–60 amps./sq. ft. Mechanical agitation is essential with this solution, as air agitation would cause frothing. The *p*H value of the solution depends on the buffer used, but is usually between 4·0 and 5·0.

A process of the United States Rubber Company(10) employs a Watts solution containing 0·5–2·0 g/l of a reaction product of sulphuric acid with 2-mercapto- 6-methyl- 4, 6-diethylhydropyrimidine, while the Monsanto Chemical Company(11) employs a mixture of polysulphonates of isomeric diphenyl benzenes which boil at 369°C. This brightener is present in a Watts nickel solution to the extent of 3·5 per cent., or may be used in a hydrogenated form in which 40–70 per cent. of its double bonds have been saturated.

. A recent process patented by the Seymour Manufacturing Company (12) employs a Watts nickel solution with the addition of o-sulphobenzaldehyde or other sulphonated aldehyde containing the —SO_3X group where X is either hydrogen, a metal, or a cation such as an amine. To this solution may be added two other addition agents, namely, a sulphonic acid (e.g., 1–10 g/l naphthalene 1,5-disodium sulphonate) and 0·5–1·5 g/l of thiourea or a derivative. Good results are stated to be achieved by the following solution :

Nickel sulphate	37 oz./gall.
Nickel chloride	8 „
Boric acid	5 „
Naphthalene 1,5-disodium sulphonate...	2 „
o-sulphobenzaldehyde	3 „
Thiourea	0·05 „

This solution works best at *p*H 3·5–4·0 (electrometric) and at temperatures of 115°–120°F., using current densities of 30–50 amps/sq. ft. Thiourea may be replaced by derivatives, e.g., allylthiourea, ethylthiourea, phenylthiourea, etc.

PLANT CONTROL

The plant layout employed with organic bright nickel solutions is similar on the whole to that used with the cobalt-nickel baths.

Rubber-lined tanks are employed and it is important that the rubber is of the proper quality and not attacked by the hot bright-nickel solution. Suitability may be ascertained by immersing a strip of the rubber lining in the hot solution in a beaker, from which nickel is subsequently deposited on a bent steel strip, to demonstrate the quality and adhesion of the plate in various current density areas.

The temperature of the electrolyte is maintained by heating coils, or alternatively, from a heat exchanger made of duriron, carbon or glass; lead may be used only in low chloride solutions. The filtration unit may be separate or included in the heat exchanger.

The usual rules for stopping-off plating racks apply in continuous bright nickel-chrome plating plants, to prevent contamination of the electrolyte. Contaminants of bright-nickel solutions may include copper, lead, tin, iron, aluminium and chromic acid, and in some cases also alkali metals and ammonium salts. Solutions may be purified by low current density treatment or by precipitation in the manner described in Chapter 3. Organic contaminants may be removed by treatment with activated carbon.

Organic type bright nickel solutions are generally operated at between *p*H 2–4, i.e., at lower *p*H values than cobalt-nickel solutions. Pitting is therefore more frequent and cannot be controlled with hydrogen peroxide, as this affects the brightness. Hence the common use of wetting agents to reduce the surface tension of the solution.

THEORY OF ORGANIC BRIGHT NICKEL SOLUTIONS

The authors of bright nickel processes frequently claim that as well as maintaining the smoothness and lustre of a highly polished basis metal, deposits on dull surfaces actually become brighter with increase in thickness. The mechanism by which this is caused is complex and has not yet been fully explained. Interesting work has, however, been done in this field by G. E. Gardam and A. W. Hothersall([13]), who have investigated the brightening action as well as the physical properties and structure of bright nickel deposits.

Sections of organic bright nickel deposits do not show any clear structure and differ from the fine structure which is observed in cobalt-nickel deposits. A large number of lines parallel to the metal surface are discernible and these are thought to be due to periodic variations in current density.

Experiments on stress and hardness of bright nickel deposits were carried out on deposits from three solutions, consisting of a Weisberg-Stoddard solution, and Watts solutions containing naphthalene trisulphonate, and propyl naphthalene sulphonic acid respectively. Only the solution containing naphthalene trisulphonate produced stress-free deposits, and hardness tests gave the following values :

	*p*H	*Hardness No.*
NSB.KC* solution	3	190 D.P.H.
„ „	5·8	260 „
Weisberg-Stoddard solution		430 „
NSB.KC and Naphthalene Trisulphonate		545 „
NSB.KC and Propyl Naphthalene Sulphonic Acid		544 „

The effect of naphthalene trisulphonate on hardness and appearance of a nickel deposit was investigated in a NSB.KC solution at *p*H 4·6, a bath temperature of 35°C. and at current density of 15 amps./sq. ft. In these experiments, where concentrations up to 5 g/l naphthalene trisulphonate were present, the Diamond Pyramid Hardness value increased from 167 to 523, and fully bright deposits were obtained only at the highest hardness figures at concentrations of above 1·0 g/l of the brightener.

With the solutions used, Gardam and Hothersall also found that the lustre of deposits formed on smooth surfaces of very small grain size is independent of thickness, but on surfaces of large grain size, (i.e., etched or bright annealed and unpolished) only semi-lustrous deposits were obtained with thin deposits, while brightness increased with thickness of deposit. Similarly, a soft, dull nickel deposit began to show lack of lustre at a smaller grain size when

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[*] The NSB.KC solution contains 240 g/l nickel sulphate, 30 g/l boric acid and 20 g/l potassium chloride.

formed on a lustrous surface of large rather than of small grain size.

Later investigations by G. E. Gardam(14,15) were concerned with smoothing action and these were carried out on serrated cathodes on which various thicknesses of bright nickel were deposited. The results showed that there are two distinct smoothing actions; one showed particularly by solutions containing cadmium or zinc, which caused a large-scale smoothing, and filled in the serrations on the cathode; the other, a sub-microscopic smoothing action which produces brightness. Most brighteners commonly used, including sulphonates, possessed only the latter smoothing action, filling in microscopic hollows and changing the shape of the surface to produce specular reflectance. The fact that slightly matt deposits are brightened quickly at first and then more slowly, tended to confirm this.

Solutions containing cadmium or zinc, on the other hand, produced very quick brightening on rough deposits, and while the final result is often not fully lustrous, the rate of brightening, in some cases, increased with increase in thickness, suggesting that this action results in filling the larger hollows without affecting, or even increasing tiny corrugations.

Deposits formed in the presence of a sulphonate contain in some cases up to 6·4 per cent. sulphur and 0·2 carbon, and the mechanism of adsorption of the organic compound in the nickel deposit was investigated by Gardam in various experiments with sulphonate solutions. The production of a fine-grained deposit produced in this way was found, however, to be incidental to, and not the main cause of, brightening, which is ascribed to the smoothing action described above, and is caused, most probably, by preferential inclusion of sulphonate on the crests rather than the hollows of the surface and the resulting increased deposition potential on these high spots.

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Am. Soc. Met.	American Society for Metals
Am. Soc. Test. Mat.	American Society for Testing Materials.
Anales fís. y quím.	Anales de física y química (Madrid)
Anales Soc. españ. fís. quim.	Anales de la sociedad española de física y química.
Ann. Physik	Annalen der Physik.
Ann. Sect. platine, Inst. Chem. gén. U.R.S.S.	Annales du secteur de platine et des autres métaux précieux, Institute de chimie général (U.R.S.S.)
Arkiv. Kemi, Mineral Geol.	Arkiv för Kemi Mineralogi och Geologi.
Automobile Eng.	Automobile Engineer.
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'académie des sciences de Russie.
Bull. Soc. Chim.	Bulletin de la société chimique de France.
Bull. Soc. Chim. Belg.	Bulletin de la société chimique de Belgique.
Bull. Soc. Françe Mineralogie	Bulletin de la société française de minéralogie.
Can. Chem. Process Inds.	Canadian Chemistry and Process Industries.
C.A.	Chemical Abstracts (American).
Chem. App.	Chemische Apparatur.
Chem. Listy	Chemické Listy pro védu a prûmysl. sum.
Chem. News	Chemical News.
Chem. Zentr.	Chemisches Zentralblatt.
Chem. Ztg.	Chemiker Zeitung.
City Coll. Vect.	City College Vector (School of Technology, New York).
Compt. rend.	Comptes Rendus.
Compt. rend. Congr. Intern. Eléc.	Compte Rendu du Congrès international de l'élétricité.
Deut. Goldschmiedeztg.	Deutsche Goldschmiede-Zeitung.
Eng. Mat. & Intern. Power Rev.	Engineering Materials and International Power Review.
Ind. Bull. (Arth. D. Little)	Industrial Bulletin (Arthur D. Little Inc.)
Jap. J. Eng. Abs.	Japanese Journal of Engineering (Abstracts).
Jernkontorets Ann.	Jernkontorets Annaler.
J. Appl. Chem. U.S.S.R.	Journal of Applied Chemistry (U.S.S.R.) (Zhurnal Prikladaoĭ Khimii).
J. Appl. Phys.	Journal of Applied Physics.
J. Electrodep. Tech. Soc.	Journal of the Electrodepositors' Technical Society.
J. Franklin Inst.	Journal of the Franklin Institute.

J. Indian Chem. Soc.	Journal of the Indian Chemical Society.
J. Inst. Met.	Journal of the Institute of Metals.
J. Opt. Soc. Am.	Journal of the Optical Society of America.
J. Phys. Chem.	Journal of Physical Chemistry.
Khim. Referat Zhur.	Khimichenskiĭ Referationyĭ Zhurnal.
Kolloid Z.	Kolloid-Zeitschrift.
Met. Clean. & Fin.	Metal Cleaning and Finishing.
Met. Fin.	Metal Finishing.
Met. Ind. (London)	Metal Industry (London).
Met. Ind. (N.Y.)	Metal Industry (New York).
Met. Progr.	Metal Progress.
Met. Treatm.	Metal Treatment.
Met. Eng. Dig.	Metallurgical Engineer (Digest).
Metallwaren–Ind. u. Galvano–Tech.	Metallwaren–Industrie und Galvano–Technik.
Met. & Alloys	Metals and Alloys.
Mitt. Forsch. Inst. u. Probieramts Edelmetalle Staatl. höheren Fachschule schwäb. Gmünd	Mitteilungen des Forschungs–Instituts und Probieramts für Edelmetalle und der Staatlichen höheren Fachschule schwäbisch Gmünd.
Mon. Rev. Am. Electroplat. Soc.	Monthly Review of the American Electroplaters' Society.
Oberflächentech.	Oberflächentechnik.
Oesterr. Chem. Ztg.	Oesterreichische Chemiker Zeitung.
Phil. Mag.	Philosophical Magazine and Journal of Sciences.
Phys. Rev.	Physical Review (American Institute of Physics).
Phys. Z.	Physikalische Zeitschrift.
Polytech. Weekblaad	Polytechnisch Weekblaad.
Proc. Am. Electroplat. Soc.	Proceedings of the American Electroplaters' Society.
Proc. Indiana Acad. Sci.	Proceedings of the Indiana Academy of Science.
Proc. Intern. Electrodep. Conf.	Proceedings of the International Conference on Electrodeposition.
Prod. Fin.	Products Finishing.
Przemysl Chem.	Przemysl Chemiczny (Chemical Industry, Poland).
Rev. gén. éléc.	Revue génerale de l'élétricité.
Rev. Mét.	Revue de Métallurgie.
Sci. Quartl. Natl. Univ. Peking	Science Quarterly, from the National University of Peking.
Soc. Chim. Phys.	Société de Chimique Physique.
Tech. Repts. Tôhoku Imp. Univ.	Technology Reports of the Tôhoku Imperial University.
Tech. Zentr. Prakt. Metallarbeit	Technisches Zentralblatt für Praktische Metallbearbeitung.
Trans. Am. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Electrochem. Soc.	Transactions of the Electrochemical Society.
Trans. Far. Soc.	Transactions of the Faraday Society.
Trans. Illinois State Acad. Sci.	Transactions of the Illinois State Academy of Science.

Trans. Kansas State Acad. Sci. ...	Transactions of the Kansas State Academy of Science.
Trudy Konferentsiĭ Korroziĭ Metal...	Trudy Konferentsiĭ po Korroziĭ Metallov.
Tsevetnye Met.	Tsevetnye Metalli (Non-ferrous Metals).
Vestnik Inzhenerov i Tekh.	Vestnik Inzhenerov i Tekhnikov (Engineers' and Technicians' Review).
Wire and Wire Prod.	Wire and Wire Products.
Zapiski Inst. Khim. Akad. Nauk, U.S.S.R.	Zapiski Institutu Khimiï Akademiya Nauk, U.S.S.R.
Zavodskaya Lab.	Zavodskaya Laboratoriya (Factory Laboratory).
Z. Elektrochem.	Zeitschrift für Elektrochemie und angewandte Physikalische Chemie.
Z. Metall–u. Schmuckwaren–Fabrik. sowie Verchrom.	Zeitschrift für Metall–und Schmuckwaren Fabrikation sowie Verchromung.
Z. Metallkunde	Zeitschrift für Metallkunde.
Z. Physik	Zeitschrift für Physik.

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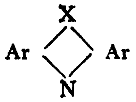

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83. W. J. HARSHAW & K. E. LONG, *U.S.* 2,299,054 (1942).
Co-depositing selenium or tellurium and preparing this deposit for chromium plating by making anodic, then cathodic in solution containing sodium cyanide, carbonate and formate.

84. A. POLLACK, *Oberflächentech.* **19**, 91-2 (1942); *Chem. Zentr* 1943, *I*. 582.
Effect of sodium sulphate. Also addition of cadmium chloride and phenol-sulphonate to Watts solution.

85. D. V. STEPANOV & I. P. LYASHCHENKO, *Russ.* 55,547 (1939).
Nickel chloride-boric acid solution with an oxide, hydroxide or carbonate of nickel, and a sulphonated naphthalene.

86. R. O. HULL & F. RUEBENSAAL, *U.S.* 2,312,097 (1943).
Watts solution containing 1–5 g/l sulphite cellulose waste and 1-3 g/l methyl naphthalene mono-sulphonic acid or a salt.

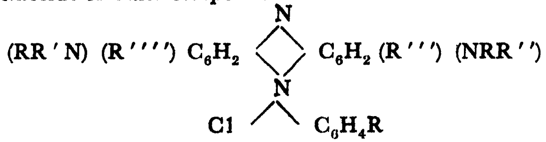
87. HOUDAILLE, HERSHEY CORP. *U.S.* 2,312,517 (1943).
Semi-bright deposits from chloride or sulphate nickel solutions containing 0·5 g/l lead, and sodium formate as carrier for maintaining lead in solution.

88. P. LIND, W. J. HARSHAW & K. E. LONG. *U.S.* 2,315,802 (1943).
Two addition agents: (1) 0·002 g/l alkaloid, *e.g.*, caffeine, quinine, Brucine, etc. (2) 0·2 g/l naphthalene sulphonate or aryl sulphonamide or sulphimide.

89. A. WESLEY & J. CAREY, *U.S.* 2,316,303 (1943).
Semi-bright nickel on iron and steel; various details.

90. H. BROWN, *U.S.* 2,321,182 (1943).
An aliphatic polychlorinated or polybrominated aldehyde, *e.g.*, bromal aldehyde or butyl chloral hydrate, in nickel solution.

91. P. LIND, W. J. HARSHAW & K. E. LONG, *U.S.* 2,326,999 (1943).
Two addition agents: (1) ms-phenyldiamino diphenyl azonium chloride or other compound of formula:



R, R′, R″, R‴, R⁗ = H, Me or Et.

(2) o–benzoic sulphimide or one of its salts with sodium, potassium, nickel, iron or cobalt.

92. W. P. TER HORST, *U.S.* 2,361,720 (1944), *Can.* 425,193 (1945).
Nickel solution containing the reaction product of an alkyl–2–mercaptodihydroxypyrimidine with sulphuric acid.

93. W. L. PINNER & R. B. KINNAMAN, *Mon. Rev. Am. Electroplat. Soc.*, **32**, 277-84 (1945).
High concentration of nickel chloride for high speed plating. Brighteners are given as well as conditions for semi-bright deposition.

94. B. MARTIN, *Mon. Rev. Am. Electroplat. Soc.*, **33**, 498-500 (1946).
Organic type bright nickel solutions.

95. M. B. DIGGIN, *Mon. Rev. Am. Electroplat. Soc.*, **33**, 500-4 (1946).
Alloy type bright nickel solutions.

96. C. B. F. YOUNG & C. STRUYK, *Trans. Electrochem. Soc.*, **89**, 31 *pp.* (*preprint*), (1946).
Cobalt-nickel deposition from chloride solutions buffered with boric acid. Bright and semi-bright.

97. H. BROWN, *U.S.* 2,240,801 (1946).
A salt of thallium (sulphate, fluoride, chloride, carbonate etc.) with an aryl compound containing $=C—SO^{+}$—linkage where sulphur is

positively valent and bound to an oxygen atom, *i.e.*, aryl sulphonamides, sulphonates or sulphinates. See also *Brit.* 564,232 (1944) for similar solution containing tellurium.

98. M. KOSMIN, *U.S.*, 2,401,428 (1946).
3·5% of a mixture of polysulphonates of isomeric diphenyl benzene is used as addition agent

99. M. B. DIGGIN & O. KARDOS, *Met. Fin.* **44**, 429-32 (1946).
Bibliography of electrodeposited nickel alloys.

100. M. L. FREED, *U.S.* 2,409,119 (1946).
Sulphonated aryl aldehydes are used as brighteners, *e.g.*, o–sulphobenzaldehyde.
U.S. 2,409,120, M. L. FREED AND O. A. STOCKER.
A sulphonated aryl brightener free from aldehyde is added as well as thiourea or a derivative, to improve ductility.

101. R. O. HULL & R. A. HOFFMAN, *U.S.*, 2,417,203 (1947).
A sulphurised protein, prepared by carbon disulphide treatment of an enzyme hydrolysed protein (*e.g.*, gelatin, glue, etc.), is used together with o-sulphobenzaldehyde, etc.

See also: 3, 5, 9, 11, 12, 16, etc. See also *Brit.* 584,977 (1947).

3. ZINC.

102. HIROTA SATO, *Hokkô* 1926 (22), 11-24, *Jap J. Eng. Abs.* **6**, 86 (1928), *J. Inst. Met.* **41**, 571-2.
Organic addition agents to zinc plating solutions.

103. C. J. WERNLUND, *Mon. Rev. Am. Electroplat. Soc.* **17**, *No.* 11, 4-9 (1930).
Cadmium-zinc alloy from cyanide solution containing 85–92% zinc, 8–15% cadmium.

104. S. WERNICK, *Compt. rend. Congr. Intern. Elec.* **9**, 118-22 (1932).
Review of zinc and cadmium plating.

105. E. F. HOFF, *Met. Clean and Finish.* **7**, 483-6, 490 (1935); **8**, 169-73 (1936).
Comparison between cadmium and zinc plating, bright plating, etc.

106. HANSON–VAN WINKLE–MUNNING CO. *Can.* 359,945.
Bright zinc plating in a cyanide solution containing aldehydes or ketones.

107. E. F. HOFF, *U.S.* 2,080,479 (1937).
Cyanide solution containing a soluble compound of manganese or rhenium, *e.g.*, manganous sulphate, potassium rhenate or manganous cyanide.

108. R. O. HULL, *U.S.* 2,080,483 (1937).
Cyanide solution containing thiourea, cobalt sulphate, nickel sulphate or phenylthiourea.

109. F. A. WESTBROOK, *U.S.* 2,080,520 (1937).
Cyanide-zinc solution containing a soluble compound of uranium, tungsten or molybdenum.

110. J. A. HENRICKS, *U.S.* 2,101,580 (1937).
Cyanide solution containing a soluble ammonium thio-cyanate formaldehyde resin.
U.S. 2,101,581, relates to thiourea formaldehyde resins.

111. Drew, *Steel*, **100**, No. 25, 66-70 (1937).
Bright zinc on steel. The process of the Republic Steel Corporation is described.

112. E. I. du Pont de Nemours & Co. Inc. *Fr.* 826,935 (1938).
A cyanide solution containing a heterocyclic compound containing oxygen, *e.g.*, coumarine, furan or derivatives, morpholine or diphenylene oxide. Preferably also a compound of molybdenum, chromium, tungsten, uranium, manganese, rhubidium, rhenium, iron, cobalt or nickel.

113. R. Spears, *J. Electrodepos. Tech. Soc.* **14**, 4 *pp.* (*preprint*), (1938).
Bright zinc processes, as well as bright dips for dull zinc plating.

114 E. Armstrong, *Met. Treatment*, **4**, 71-6 (1938).
Physical properties and corrosion resistance of bright zinc deposits.

115. R. A. Hoffman, *Brit.* 490,145 (1938).
Cyanide solution containing sodium thiosulphate, free from other metals.

116. *A.E.S. Proc. Am. Electroplat. Soc. June*, 1938, 91-9.
Experiments with addition agents to cyanide solutions are described. Turkey-red oil, bran, gum arabic, ammonium molybdate and phenol were not satisfactory. Gelatin (2–4 g/l) gave fairly bright deposits in agitated solutions.

117. H. Fisher & H. Baerman, *Korrosion und Metallschutz*, **14**, 356-64 (1938).
Various processes are discussed and physical properties of deposits studied.

118. L. S. Mkhitar'yan, *Aviapromyshlennost* (1938), *No.* 11, 29-32; *J. Inst. Met.* **66**, *Pt.* 2, *Met. Abs.* **7**, 74.
Bright zinc on steel and brass, from a cyanide solution containing glycerol; wash after plating in 3–6% nitric acid.

119. H. J. Barret & C. J. Wernlund, *U.S.* 2,171,842 (1939).
1 g/l or less polyvinyl alcohol as brightener.

120. C. H. Senter & R. Taft, *Trans. Kansas. Acad. Sci.* **42**, 237-40 (1939).
Experiments on 25 organic addition agents, nine were satisfactory in acid solution: lactic-, citric-, and benzoic acid, phenol, Et-carbonate, β–naphthol, *p*–hydroxy phenyl glycine and p–hydroxybenzoic acid.

121. N. T. Kudryavtsev & A. A. Nikiforova, *Russ.* 54,826 (1939).
Acid solution containing 2,6–or 2,7–Naphthalene disulphonates.

122. E. I. du Pont de Nemours & Co., *Fr.* 848,162 (1939).
Cyanide solution containing a soluble condensation product of a phenol and an aldehyde, also a soluble compound of molybdenum, chromium, cobalt, manganese, nickel, iron, titanium, aluminium or tungsten.
See also Brit. 588,268 (1947).
A condensation product of sodium cyanide with formaldehyde is used in zinc solutions together with polyvinyl alcohol.

123. E. I. du Pont de Nemours & Co. *Fr.* 848,843 (1939).
Cyanide solution containing an aryl-alkyl ether with a –CHO group.

124. N. T. Kudryavtsev & A. A. Nikiforova, *Korroziya i Borba s Nei*, **5**, *No.* 5-6, 56-72 (1939), *Noraya a Tekhnol v. Aviastraenii, Pervoc, Glavnoe Upravlenie NKAP Kabinet Obmena Opytum po*

Noveĭ Tekhnol i Orgenizatsii Proizvodstva 1939, *No.* 4, 79-88, *Khim. Referat. Zhur* 1940. *No.* 2, 88.
A 3N solution of zinc sulphate, aluminium sulphate and sodium sulphate. 40 addition agents were investigated. The best were sodium 2, 6– and 2, 7– naphthalene disulphonate and thiourea.

125. H. KRAUSE. *Tech. Zentr. Prakt. Metallarbeit,* **49**, 232-4 (1939). *Met. Abs.* (*J. Inst. Met.*) **7**, 484 (1940).
Replacing cadmium and nickel. Elimination of impurities and review of patents.

126. J. L. BRAY & E. R. MORRAL, *Trans. Electrochem. Soc.* **78**, 8 *pp.* (*preprint*) (1940).
Amine addition agents to cyanide solutions were studied.

127. F. A. WESTBROOK, *U.S.* 2,233,500 (1940).
Cyanide solution containing oxygen-containing heterocyclic compounds, *e.g.*, Piperonal.

128. N. T. KUDRYAVTSEV & A. A. NIKIFOROVA, *Korroziya i Borba s Neĭ* **6**, *No.* 2, 44-6 (1940).
Bright deposits in presence of tin ions. Best results when tin=0·1—0·25 g/l. Mercury and lead are less effective. Excellent brightening using tin and lead.

129. N. T. KUDRYAVTSEV & A. A. NIKIFOROVA, *Trudy Soveshchaniya povoprosam Korrozii* 1940, 231-8. *Khim Referat Zhur* 1940, *No.* 7, 135.
2,7–naphthalene disulphonate in acid solution.

130. N. T. KUDRYAVTSEV & A. A. NIKIFOROVA, *Russ.* 57,509 (1940).
A stannic salt as addition agent.

131. R. O. HULL & C. J. WERNLUND, *Trans. Electrochem. Soc.* **80**, 19 *pp.* (*preprint*), 1941.
Cyanide zinc plating and bright plating.

132. M. SCHLÖTTER & H. SCHMELLENMEIER. *Korrosion & Metallschutz* **17**, 117-23 (1941).
Plating from alkali and acid, dull and bright zinc solutions.

133. R. A. HOFFMAN. *Can.* 401,286.
Vanillin, veratraldehyde, anisaldehyde, 2,3–dimethoxy benzaldehyde or o–methoxybenzaldehyde, also a soluble compound of molybdenum, chromium, manganese, cobalt, nickel, iron, tungsten, aluminium or titanium.

134. NIERAS, *Anales. Soc. españ. fis quim,* **37**, 54-7 (1941).
N. zinc perchlorate (I) M. sodium perchlorate and 0·1 N. perchloric acid solution.

135. R. A. HOFFMAN, *U.S.* 2,288,318 (1941).
Steel stampings are plated in cyanide solution containing a condensation product of an aldehyde with a phenol.

136. W. ECKHARDT, *Oberflächentech,* **18**, 170-1 (1941).
Potassium cyanide solution containing vanillin produces bright deposits with moving cathode. If iron, nickel or molybdenum are present, very bright deposits are obtained with stationary cathode.

137. W. ECKHARDT, *Korrosion & Metallschutz,* **17**, 401-3 (1941). *Sheet Met. Ind.* **17**, 109-10, 114 (1943).
American solutions were investigated. The best contained (1)

molybdic oxide and vanillin; (2) sodium acetate and nickel nitrate, with or without sodium perborate or oxalic acid and molybdic oxide.

138. F. Jelenik, *Metallwaren-Ind. Galvano-Tech.* **39**, 305-8 (1941). *Chem. Zentr.* 941 II, 2135.
The sodium hydroxide: zinc cyanide: sodium cyanide ratio should be 1 : 1 : 0·66.

139. W. Howaldt & R. Halfen, *Ger.* 714,829 (1941).
Sulphurous acid or sulphites are added to zinc plating solution.

140. R. I. Kaufmann, *Sodostroenie,* **11**, No. 8, 344 (1941); *Chem. Zentr.* 1941, II, 1791.
Cyanide solution containing sodium sulphide and glycerol. Subsequently the work is dipped in 4% nitric acid and 18% chromic acid solution.

141. J. S. Jones & P. M. Walker. *J. Electrodepos. Tech. Soc.* **17**, 155-63 (1942).
A bright zinc process is described.

142. F. Zschau, *Z. Metall-u. Schmuckwaren-Fabrik, sowie Verchrom,* **23**, 151-2 (1942). *Chem. Zentr.* 1942 II, 589.
Zinc solutions for plating on aluminium.

143. E. Beutel & A. Kutzelnigg, *Ger.* 717,360 (1942).
Alkali solution containing zinc sulphate and sodium or potassium hydroxide. *Ger.* 724,230 (1942) adds to this other zinc compounds (except zinc cyanide).

144. T. Dingman, *Ger.* 731,835 (1943).
One or more colloids and an aldehyde as addition agents.

145. B. Wullhorst. *Mitt. Forsch. Inst. Probieramts, Edelmetalle, Staatl. höheren Fachschule Schwäb, Gmünd* 1942, *No.* 7, 12-27. *Chem. Zentr.* 1943, I, 1817.
Study of the effect of sulphur and of metals: silver, nickel, selenium, uranium, iron, cobalt, mercury, cadmium, molybdenum and nickel in cyanide solutions.

146. N. T. Kudryavtsev. *Trudy. Konferentsii. Korrosii. Metal,* **2**, 175-85 (1943).
Effect of mercury, tin and lead in zincate solutions.

147. J. L. Bray and R. E. Howard. *U.S.* 2,355,505 (1944).
Bright zinc on bright annealed steel wire from a zinc sulphate solution which is 0·006 – 0·01 M with respect to pyridine.

148. Allen Gray, *Steel* **117**, *No.* 15, 108-9, 158-70; *No.* 16, 136-42; *No.* 17, 129-34; *No.* 18, 110-4; *No.* 19, 142-4, 182-6; *No.* 20, 132-6 (1945).
Comprehensive survey of zinc plating. Bright plating is one of the aspects dealt with.

149. J. Bernal, A. L. Lasheras and A. M. Tinao, *Anales fis. y quim* (*Madrid*) **41**, 1294-1302 (1945).
N solution of zinc perchlorate and sodium perchlorate and 0·25 N. aluminium perchlorate at *p*H 3, 25°C., agitated.

150. J. L. Bray and R. E. Howard. *U.S.* 2,393,741 (1946).
Zinc sulphate solution containing triethyleneamine at high current densities.

151. M. BALLAY & P. VOGT, *Métaux et Corrosion* **21**, 89-91 (1946).
A cyanide solution containing 2 g/l sodium sulphide.
See also: 4, 7, 11, 15, etc.

(4) CADMIUM.

152. C. H. HUMPHRIES. *Brit.* 309,071; 304,668 (1928).
Cyanide solution containing caramel, barley sugar, malt sugar and syrup.

153. C. H. HUMPHRIES. *Brit.* 330,289; 328,574 (1929).
Acid solution containing glue, agar agar, gelatin, sugar.

154. C. M. HOFF. *Mon. Rev. Am. Electroplat. Soc.* **17**, *No.* 6, 19-35 (1930).
Review of cadmium plating, including bright plating.

155. G. B. HOGABOOM & M. B. DIGGIN. *U.S.* 1,893,368 (1933).
Cyanide solution containing oxyheterocyclic compound, *e.g.*, hematein, furfural, alkali metal furfurate or alkali furfural resin.

156. A. RIUS & L. QUINTERO, *Anales, Soc. españ. fís. quím.* **32**, 1077-89.
Cyanide solution containing soap, (Lipofor) licorice or saponin. Both the anode and cathode become brilliant.

157. S. WERNICK, *Trans. Faraday Soc.* **31**, 1237-42 (1935).
Factors affecting structure and grain size of cadmium deposits.

158. C. M. HOFF *Met. Clean. and Fin.* **7**, 483-6, 490 (1935).
Comparison between cadmium and zinc plating, bright plating etc. *See also Met. Clean. and Fin.* **8**, 169-73 (1936); *U.S.* 2,086,226 (1937).

159. J. A. HENRICKS. *U.S.* 2,085,747 (1937).
Cyanide solution containing acetaldehyde, aldol, crotonaldehyde, paraldol, etc. *U.S.* 2,085,748. Cyanide solution containing the reaction product of an alkali cyanide with an aliphatic aldehyde or ketone, containing 2–9 carbon atoms, not more than two hydroxyl groups and free from sulphur, nitrogen or carboxylic acid groups. *U.S.* 2,085,749. A cyanide solution containing the reaction product of an alkali cyanide with a carbocyclic compound, *e.g.*, benzaldehyde, benzoin, cyclohexanone, quinone. *U.S.* 2,085,750. Cyanide solution containing an " amketaldo-resin " obtained as a prereacted addition agent by reaction of a ketaldone with an " amo " in alkali solution.

160. J. V. VAUGHEN, *U.S.* 2,085,776 (1937).
Cyanide solution containing the reaction product of a ketaldone with an amine.

161. R. O. HULL, *U.S.* 2,090,049 (1937).
Cyanide solution containing an oxidised amketaldo resin prepared by reaction of a ketaldone with an amino compound in alkali solution.

162. R. O. HULL. *Fr.* 812,729 (1937).
Cyanide solution containing the reaction product of aldehydes or ketones with amines.
J. A. HENRICKS, *Fr.* 812,730. These addition agents are hydrogenated, oxidised or halogenated.

163. G. LUTZ, *Fr.* 816,536 (1937).
Cyanide solution containing (*a*) a reduced amo-ketaldo-resin; (*b*) a reduced reaction product of a ketaldone with an alkali cyanide; (*c*) a reduced amo-ketaldo-resin and a small proportion of a metal of the iron group of at.wt.>58.

164. GRASSELLI CHEM. CO. INC. *Ger.* 670,220 (1939); *U.S.* 1,818,179 (1931).
Solutions containing a reaction product of an alkali cyanide with a ketone or aldehyde other than formaldehyde.

165. L. CAMEL, *U.S.* 2,143,760 (1939).
A cyanide solution containing sodium thiosulphite, a silver or cobalt salt, and tung oil or cod liver oil. *U.S.* 2,143,761. A cyanide solution containing sodium thiosulphite and sodium thiosulphate. (1940).

166. J. GUZMÁN & L. QUINTERO, *Anales. Soc. españ. fis quim* (5) **35**, 24-40
Plating with three electrodes. The Guzmán method (*ibid* **32**, 918 (1934)) of potential indicator is applied. Bright deposits from cyanide solutions containing a colloid and nickel.

167. F. C. MATHERS & W. J. GUEST, *Trans. Electrochem. Soc.* **78**, 2 *pp.* (*preprint*) (1940).
Glycerol 'foots', *i.e.*, the residues from the distillation of glycerol in soap manufacture, is used in cyanide solutions.

168. R. WEINER, *Ger.* 704,989 (1941).
Cyanide solution containing molybdenum, tungsten, chromium, uranium, manganese, rhenium, titanium, zirconium, hafnium, thorium, iron, cobalt or nickel, etc.

169. A. J. FUSCO & N. E. WOLDMAN, *Iron Age* **149**, *No.* 12, 46-52 (1942).
Cyanide solution containing nickel, glue, casein, sulphonated castor oil.

170. J. A. HENRICKS, *U.S.* 2,350,165 (1944).
Cyanide solution containing a condensation product of sulphuric acid with aliphatic aldehydes, *e.g.*, crotonaldehyde, aldol, paraldol, furfural. Method of preparation of the resin.

171. R. O. HULL, *U.S.* 2,383,798 (1945).
Cyanide solution containing isoamketaldo resins etc., together with a metal brightener, *e.g.*, iron, cobalt, nickel, etc., are freed from pitting by addition of 0·01–0·5% sulphonated castor oil.

See also: 4, 7, 11, 15, 103, 104, 105 etc.

(5) COPPER.

172. J. E. UNDERWOOD (see 20). A Rochelle salt solution containing lead acetate and sodium hydroxide.

173. J. E. UNDERWOOD, *Met. Clean. and Fin.* 1929, 355-6, *Met. & Alloys,* 1,474 (1929).
Bright copper on antimonial lead surfaces by adding sodium sulphate and various lead salts to solution.

174. C. J. BROCKMAN & A. L. BREWER, *Trans. Electrochem. Soc.* **69**, 6 *pp.* (*preprint*), 1935, also *ibid* **69**, 11 *pp. preprint* (1935).
Alkaline solutions containing ethanolamines.

175. B. F. LEWIS, *U.S. Pat.* 2,065,082 (1935).
Cyanide solution containing citrate, aluminium, sulphate and sodium hydroxide. Smooth semi-bright deposit.

176. P. V. STEPANOV, I. P. LYASHCHENKO & M. S. MATVEEVA, *Russ.* 42,392 (1935).
High current density plating in solution containing one mol. anthracene sulphonic acid per 400 g. copper sulphate.

177. C. J. BROCKMAN & J. H. MOTE, *Trans. Electrochem. Soc.* **73**, 4 *pp.* (*preprint*) (1938). *See also C.A.* **32**, 2434-5.
Amine copper solutions containing ethylenediamine and copper sulphate. *Ibid*, 6 *pp. preprint*: Copper sulphate solutions containing monoethanolamine and sodium oxalate were studied.

178. E. S. SARKISOV & A. T. VAGRAMYAN, *Russ.* 45,783 (1936).
High current density process in presence of rayon in agitated solution.

179. L. GREENSPAN, *U.S.* 2,195,454 (1940).
Copper sulphate—diethylenetriamine solution.
Trans. Electrochem. Soc. **78**, 4 *pp.* (*preprint* (1940).
Previous bright copper processes are discussed in comparison to bright nickel—addition of ammonium sulphate is suggested to the Brockman amine copper solution.

180. D. C. GERNES, G. A. LORENZ & S. H. MONTILLON, *Met.Ind.*(*London*) **57**, 253-6 (1940).
Bright deposits from sodium thiosulphite and pure copper chloride

181. A. I. LEVIN, S. H. SHCHERBAKOV, F. A. ZORIN, V. M. SVITSKIĬ, & R. A. GOKHINA, *J. Appl. Chem.* (*U.S.S.R.*), **13**, 686-92 (*in Fr.* 692) (1940).
Cyanide-free baths for plating on iron and steel. Bright plating.

182. A. K. GRAHAM & H. J. READ, *Trans. Electrochem. Soc.* **80**, 3 *pp.* (*preprint*) (1941).
Cyanide-Rochelle salt solution containing lead.

183. CHESTER SMITH & C. MUNTON, *Met. Fin.* **39**, 415-21 (1941).
Alkali citrate solutions instead of tartrate.

184. D. A. HOLT, *U.S.* 2,255,057 (1941).
Cyanide solution containing 0·01–1·0 g/l. of a betaine having at least one monocyclic hydrocarbon radical containing 10–20 carbon atoms, *e.g.*, trimethyl–C–cetyl–α–betaine.

185. T. G. COYLE, *Proc. Am. Electroplat. Soc.* 1941, 113-6.
Unichrome process, pyrophosphate solution is described.

186. C. J. WERNLUND, H. L. BENNER & R. R. BAIR, *U.S.* 2,287,654.
Double cyanide solution containing alkali hydroxide, thiocyanate and a carbohydrate (*e.g.*, sucrose).

187. F. L. CLIFTON & W. M. PHILLIPS, *Proc. Am. Electroplat. Soc.* 1942, 92-9.
Experiments with acid solutions and a wetting agent Triton No. 720, gave semi-bright deposits, and bright deposits with addition of molasses and thiourea.

188. C. J. WERNLUND, *U.S.* 2,347,448, *Brit.* 558,469 (1944).
Cyanide solution containing an alkali sulphocyanide (*e.g.*, NaCNS).

189. W. BRENNER, *U.S.* 2,391,289 (1945).
Copper sulphate solution at *p*H 1·0 containing an alkyl or aryl substituted thiourea, a wetting agent and dextrin to permit higher current densities.

190. W. BRENNER & C. B. F. YOUNG, *Prod, Fin.* **10**, *No.* 5, 64-6, 68, 70, 72, 74 (1946); No. 1, 76, 78, 80, 82, 84, 86, 88, 90 (1945).
Effect of urea in acid copper plating solutions.

191. E. D. WILSON, *U.S.* 2,411,674 (1946).
An acid copper solution containing ethylenediamine and lactic acid. *See also*: 4, 7, 8, 11, 12, 15, etc. *Also U.S.* 2,424,887 (1947).

(6) SILVER.

192. S. WERNICK, *Trans. Faraday Soc.*, **24**, 361-6 (1928).
Determination of "silver numbers" of colloids used to reduce grain size.

193. "GALVANICUS," *Oberflächentech,* **10**, 165-7 (1933).
Experiments with various silver solutions are described. Bright deposits are obtained with 1 g. sodium thiosulphite and 10 ml. ammonium hydroxide (28%) p. litre.

194. *Chem. Listy.* **29**, 117-8, 131-3 (1935).
Experimental data and theory of effect of agar agar and gelatin on crystal growth in a silver nitrate solution.

195. E. C. POWELL & A. R. DAVIES, *U.S.* 2,113,517 (1938).
Alkali cyanide solution containing carbon disulphide or mercaptan solution, or an alkaline salt of an aliphatic acid containing at least 8 carbon atoms, *e.g.*, sodium oleate, or of a sulphonic acid derived from an alcohol corresponding to such a compound, *e.g.*, Turkey-red oil.

196. D. WOOD, *Mon. Rev. Am. Electroplat. Soc.* **25**, 171-8 (1938).
Potassium nitrate replaces carbonates. This gives brighter deposits with carbon disulphide. The effect of carbon disulphide is discussed.

197. R. TAFT & L. M. HORSLEY, *Trans. Electrochem. Soc.* **74**, 14 *pp.* (*preprint*) (1938).
Experiments with addition agents to silver nitrate solutions.

198. B. EGEBERG & N. E. PROMISEL, *Trans. Electrochem. Soc.* **74**, 11 *pp.* (*preprint*) (1938).
The effect of carbon disulphide is discussed.

199. J. FISCHER, *Oberflächentech.* **16**, 78-81 (1938).
Theory of bright plating and experiments on addition agents.

200. R. WEINER, *Z. Elektrochem.* **45**, 743-50 (1939).
Critical review of bright silver plating.

201. R. WEINER, *Z. Elektrochem.* **45**, 757-9 (1939).
Silver chloride—sodium thiosulphate—sodium bisulphite—sodium sulphate solutions give bright deposits. Colloids have no effect on these solutions.

202. B. EGEBERG & N. E. PROMISEL, *U.S.* 2,176,668 (1940).
A cyanide solution containing a compound of formula $X-CO-NH_2$ where $X=NH_2$ (*i.e.*, urea) or substituted NH_2 group containing methyl, ethyl or acetyl groups.

203. R. LIEBETANZ, *Oberflächentech.* **17**, 25 (1940).
The effect of carbon disulphate in potassium cyanide solutions is discussed. Derivatives of thiocarbamic acids are recommended.

204. L. I. GILBERTSON & F. C. MATHERS, *Trans. Electrochem. Soc.* **79**, 4 *pp.* (*preprint*) (1941).
Hydroxyamides of guanidine and ethylenediamine as substitutes for cyanide solutions give bright and ductile deposits.

205. J. FISCHER & E. PÜHL, *Ger.* 731,961 (1943).
Turkey-red oil, potassium xanthate and a nickel cyanide compound as addition agents to the silver nitrate cyanide silver solution.

206. R. WEINER, *Metallmittschaft,* **22**, 472-4 (1943).
Addition of selenium (as a selenide) to cyanide solution.

207. JOHNSON MATTHEY & CO. *Brit.* 567,428 (1945).
Cyanide solution containing potassium carbonate at *p*H 12·6–13·4 gives bright deposits under given conditions.
See also: *Can.* 432,157.

208. I.C.I. LTD. *Brit.* 585,107 (1947).
A cyanide solution containing sulphur compounds, *e.g.*, 2–mercapto benzothiazole, 2–mercaptothiazole, etc.

See also: 4, 6, 7, 8, etc.

(7) TIN.

209. P. R. PINES, *Mon. Rev. Am. Electroplat. Soc.* **20**, No. 19, 49-52 (1934).
Addition agents to control crystalline growth. The solution contains stannous and stannic ions as well as sulphuric acid.

210. M. SCHLÖTTER, *Brit.* 443,429 (1936). *Fr.* 790,884.
Acid solution containing (1) lyophilic and (2) lyophobic colloids. (1) Glue, gelatin, agar agar; (2) resins, sulphonated oils, bitumen, wood tar, cellulose derivatives. High mol. wt. dyes, *e.g.*, congo red, benzopurpurin, etc. may be added, as well as dioxan for dispersion properties.

211. V. I. LAINER, *Vestnik Inzhenerov i Tekh.* (1940), 538-40.
Acid tin solutions containing surface active materials (*e.g.*, phenol, cresol).

212. A. F. ALABYSHEV & V. I. ZHUKOVA (*Trudy Leningrad, Krasnoznamenskog Khim. Tekhnol. Inst.* 1940, *No.* 8, 157-72. *Khim. Referat Zhur.* 1940, *No.* 8, 84.
Tin plating from a fused electrolyte.

213. M. SCHLÖTTER, *U.S.* 2,271,209 (1942).
Silver solution containing an aryl sulphonate of tin containing colloidally dispersed phenolic resins and glue in proportion to form electro-positive colloidal aggregates.

214. J. ANDREWS, *U.S.* 2,399,194 (1946).
Sulphoxides are added to the solution, *i.e.*, compounds of formula OHR. SOR′OH. where R & R′ are a benzene or a naphthalene group, *e.g.*, bis(*p*-hydroxyphenyl) sulphoxide and bis(hydroxynaphthyl) sulphoxide.

See also: 10, etc.

THE ELECTRODEPOSITION OF THE METALS OF THE PLATINUM GROUP.

(1) PLATINUM.

215. C. W. KEITEL, *U.S.* 1,779,436 (1930); *Fr.* 698,153; *Ger.* 549,775.
Metal deposited from platinum, palladium or rhodium baths is replaced by the addition of an amminonitrite of the metal in ammoniacal solution.

216. H. E. Zschiegner, *U.S.* 1,779,457 (1930).
A heat treated aqueous solution of the platinum group metal chloride with excess sodium nitrite and ammonia, is used as the plating solution.

217. C. W. Keitel & H. E. Zschiegner, *Trans. Electrochem. Soc.* **59**, 4*pp.* (*preprint*) (1931).
The chloride plating bath is not satisfactory because of its short life. Good bright adherent deposits from the new diamminonitrite solution. Excellent throwing power, for platinum and palladium solutions.

218. J. Rossman, *Met. Ind.* (*N.Y.*), **29**, 245-6 (1931).
Some recently patented solutions for platinum, rhodium and iridium are described.

219. Baker & Co. Inc. *Ger.* 529,848 (1930).
Deposition of platinum group metals singly, or as alloys, from a halogen free, di- or tetra-amminonitrite solution. The electrolyte, *e.g.*, platinum diamminonitrite is prepared by treating chlorplatinic acid or sodium chlor-platinate with sodium nitrite.

220. H. S. Booth & M. Merlub-Sobel, *J. Phys. Chem.* **35**, 3303-21 (1931)
Plating from anh. ammonia at its B.P. An electrolysis cell for high pressure is described.

221. B. Bart, *U.S.* 1,837,193 (1931).
An insoluble anode of electrodeposited nickel is used with a platinum phosphate solution.

222. Baker & Co. Inc. *Brit.* 348,919 (1930).
Preparation of electrolyte by adding sodium nitrate to chlorplatinic acid, palladium chloride or rhodium chloride and heating till the colour changes.

223. Shao-Tze Leo & Tsing-Nang Shen, *Science Quart. Natl. Univ. Peking*, **3**, 7-19 (1931).
Copper dishes are plated in a phosphate bath as substitute for platinum ware.

224. A. Powell, A. W. Scott, Johnson Matthey & Co., Ltd., *Ger.* 606,052 (1934); *Fr.* 731,088 (1932); *Brit.* 363,569 (1931), *U.S.* 1,901,531 (1933).
Brilliant deposits of platinum from alkali platinate solution containing a conducting salt, a stabilizing salt and an alkali hydroxide.

225. W. C. Heraeus. *Ger.* 564,088 (1931).
Platinum group metals are deposited from neutral aqueous solution of a double nitrite of sodium or potassium and the metal. Prepared by action of sodium nitrate on the double chloride. An alkali citrate or excess sodium nitrite is added to increase conductivity.

226. G. Grube & D. Beischer, *Z. Elektrochem.* **39**, 38-45 (1933).
Experiments with various solutions. The best three were: (1) Platinum chloride and trisodium phosphate; (2) Platinum chloride and triammonium phosphate; (3) Ammoniacal solution of diamminonitrite.

227. A. R. Powell, E. C. Davies & A. W. Scott (Johnson Matthey & Co. Ltd.), *U.S.* 1,906,178 (1933).
Alkaline solutions containing sodium sulphate and readily soluble crystalline alkali platinates.

228. A. WOGRIN, *Metallwaren-Ind. u. Galvano-Tech.* **31**, 90-2, 109-10, 172-3, 215-7, 234-6, (1933).
Composition and working conditions of silver, gold, platinum, palladium and rhodium plating solutions.

229. H. KRAUSE, *Feinmechanik u. Präzision* **41**, 106-8 (1933).
A review of platinum, palladium, gold, silver, rhodium, iridium, molybdenum and tungsten plating.

230. A. E. W. SMITH, *Met. Ind.* (*London*) **43**, 201-2 (1933).
Corrosion tests on electroplated platinum and reflective power of coatings.

231. I. I. ZHUKOV, *J. Gen. Chem.* (*U.S.S.R.*) **3**, 958-62 (1933).
Electrochemical properties of smooth electrolytically deposited platinum group metals.

232. MOND NICKEL CO. LTD. & A. R RAPER, *Brit.* 408,244 (1934).
Platinum, rhodium, palladium and their alloys are deposited from alkaline solutions of their amminocyanides or similar compounds in which ammonia is replaced by an organic amine. Methods of preparation are given.

233. MOND NICKEL CO. LTD. *Fr.* 764,879 (1934).
Platinum group metals are deposited from amminocyanide solution. A rhodium bath is prepared by dissolving rhodochloropentammine in aqueous sodium hydroxide, treating with potassium cyanide or hydrogen cyanide and acidifying with nitric acid.

234. E. M. WISE, *U.S.* 1,970.950 (1934).
In the use of a complex nitrite solution of sodium, potassium, nickel, barium, calcium, strontium or magnesium, aluminium, and the platinum group metal, the ratio of nitrite to platinum is 4 : 1 – 6 : 1.

235. E. M. WISE, *U.S.* 1,991,995 (1935).
Platinum group metals are deposited from solutions of their ammino cyanides.

236. MOND NICKEL CO. LTD. & R. H. ATKINSON. *Brit.* 419,819 (1934).
Platinum group metal deposits are stripped in molten sodium cyanide.

237. A. R. POWELL & E. C. DAVIES. *U.S.* 2,027,358 (1936).
Platinum, palladium and rhodium are deposited from double sodium nitrite solutions slightly acidified with sulphuric acid or phosphoric acd.

238. H. W. WHISTON, G. H. B. MCIVOR & F. W. N. THEIN, *U.S.* 2,044,415 (1936).
Apparatus for plating gold, silver or platinum on threads.

239. G. L. FINCH & C. H. SUN, *Trans. Faraday Soc.* **32**, 852-63 (1936).
Electron diffraction study of the structure of electrodeposits. Platinum was among the deposits investigated.

240. K. SCHUMPELT, *International Electrodep. Conf.* 1937, *Advance Copy* 6 *pp.*
Brief notes on platinum plating from platinum amminonitrite solutions and rhodium plating from rhodium sulphate and phosphate solutions.

241. E. C. Davies, A. R. Powell, *International Electrodep. Conf.* 1937, *Advance Copy, 7 pp.*
Platinum plating from alkaline solutions containing sodium hydroxide, sodium oxalate and sodium sulphate.

242. R. H. Atkinson, *International Electrodep. Conf.* 1937, *Advance Copy,* 14 *pp.*
Historical and general survey of platinum plating.

243. H. S. Lukens, *U.S.* 2,096,434 (1937).
Chromium steel penpoints are plated with platinum then with gold.

244. B. Egeberg & N. E. Promisel, *Met. Clean. & Fin.* **9,** 919-22, 1003-6, 1028.
Uses of metals of platinum group ; methods of testing and stripping deposits.

245. O. Kramer, *Metallwaren-Ind. u. Galvano-Tech.* **36,** 31-3 (1938).
Operating temperatures of electroplating baths. Platinum and Khananov, *J. Appl. Chem.* (*U.S.S.R.*) **10,** 1969-78 (*in Fr.* 1978-9 (1937).
Platinum and palladium plating on copper. Various methods are described.

246. O. E. Zoyagintsev, L. K. Amosova, A. Vorob'eva & N. M. rhodium are dealt with.

247. J. B. Kushner, *Prod. Fin.* **4,** *No.* 6, 46-8, 50 (1940).
Tested formulae for precious metal plating solutions, including platinum, rhodium and palladium.

248. K. Schumpelt, *Trans. Electrochem. Soc.* **80,** 10 pp. (*preprint*) (1942).
Of the six platinum metals, only rhodium is plated on a commercial scale. Details of composition for rhodium, platinum and palladium.

249. M. A. Klochko & E. S. Medvedeva, *Ann. Secteur platine, Inst. Chem. gén.* (*U.S.S.R.*) *No.* 19, 103-18 (1943).
Review of platinum and palladium plating with a short section on rhodium. 63 references.

250. H. M. Haberman, *Met. Fin.* **45,** No. 1, 56-8 (1947).
Plating with platinum, palladium and rhodium. Processes are described. 9 references.

See also : 254, etc.

(2) PALLADIUM.

251. Mond Nickel Co. Ltd. *Fr.* 738,450 (1932). *See also Intern. Nickel Co., U.S.* 1,981,715 (1934).
Insoluble anode in vat containing diaphragm. The ammoniacal solution round anode is free from metal. The solution round cathode is an ammoniacal solution of one or more compounds (*e.g.*, pallado-amine chloride).

252. Mond Nickel Co. Ltd. & A. Raper, *Fr.* 737,752 ; *Brit.* 381,932 ; *Ger.* 587,807 (1933). Use of palladium anode in palladonitrite solution in the presence of a halide.

253. Precious Metal Development Co. Inc. *Brit.* 370,539 (1931).
Alloy palladium-rhodium deposition.

254. A. R. POWELL, E. C. DAVIES AND JOHNSON MATTHEY & CO. LTD., *Brit.* 367,587 (1931).
Pallodosammine compound the acid group of which is not reduced under plating conditions, *i.e.*, the sulphate, nitrate, phosphate etc. *Brit.* 367,588 refers to similar solutions for platinum, rhodium and alloys.

255. G. GRUBE & D. BEISCHER, *Z. Elektrochem.* **39**, 131-9 (1933).
Palladium plating from potassium palladium cyanide electrolytes.

256. R. H. ATKINSON & R. A. RAPER, *J. Electrodep. Tech. Soc.* **8**, 20 *pp.*, (*preprint*) (1933).
Detailed description of processes.
Also in *Met. Ind.* (*London*) 595-8 (1933).

257. A. R. POWELL, E. C. DAVIES, *U.S.* 1,921,941 (1933).
Tetrammine palladium salt, *e.g.*, sulphate with sodium sulphate or sodium nitrate, ammonia, and a colloid, *e.g.*, 0·01% dextrin.

258. B. BART, *U.S.* 1,947,180 (1934).
Silver articles are plated successively with nickel-palladium-rhodium.

259. R W. HARBINON, *Deut. Goldschmiedztg* **37**, 32-4 (1934); *Met. Abs.* (*in Met. & Alloys*) **5**, 273.
Porosity of palladium deposits. Best base metals are silver, copper and copper alloys. Methods of plating and cleaning.

260. SOC. D'UTILISATION DES MÉTAUX, *Fr.* 780,711 (1935).
Iron, nickel, steel or bronze are plated with cobalt then with chromium, palladium, rhodium or iridium. Especially for moulds for glass, rubber or plastics.

261. A. R. RAPER, *U.S.* 1,993,623 (1935).
A potassium palladonitrite solution, using a palladium anode.

262. J. FISCHER & H. BARTH, *Ger.* 698,194 (1940).
Bright palladium deposits from a solution at *p*H 10–14, free from cyanide and ammonia.

263. MOND NICKEL CO. LTD. *Brit.* 544,534 (1942).
Palladium chloride solution at *p*H <2·1, preferable 0–0·5.

264. M. A. KLOCHKO & Z. S. MEDVEDEVA, *J. Appl. Chem.* (*U.S.S R.*) **15**, 25-46 (1942).
History of palladium plating. Various solutions are discussed.

265. G. C. LAMBROS, *Met. Fin.* **41**, 73-6 (1943).
Description of "Pallite" process.

266. K. SCHUMPELT, *Mon. Rev. Am. Electroplat. Soc.* **30**, 60-2 (1943).
Plating with precious metals in war time. Rhodium for reflectors, palladium as substitute for platinum.

267. J. FISCHER, *Ger.* 726,204 (1942).
For moulded metals coated with noble metals an undercoat is used of $>5\mu$ palladium, deposited from a solution at *p*H 10-14, free from cyano salts.

268. E. M. WISE & R. F. VINES, *U.S.* 2,335,821 (1943).
A chloride solution containing ammonium chloride and hydrochloric acid. Numerous details.

See also: 215, 216, 217, 219, 222, 228, 229, 231, 232, 233, 234, 235, 236, 237, 244, 246, 247, 248, 249, 250, etc.

(3) RHODIUM.

269. L. Cinamon, *Brass World*, **28**, 971 (1932).
Compositions of sulphate and phosphate baths.

270. C. G. Fink & G. C. Lambros, *Trans. Electrochem. Soc.* **63**, 6 pp. (*preprint* (1933); *Met. Ind.* (*N.Y.*) **31**, 208-9 (1933).
The use and preparation of rhodium plating baths based on rhodium hydroxide. An ammonium sulphate solution was best.

271. Prec. Met. Devel. Co. Inc., *Brit.* 374,002 (1932).
Rhodium plating on silver, especially for reflectors for ultra-violet light. The solution contains rhodium ammonium nitrite. The base metal is silver, copper, nickel or palladium.
Brit. 374,003, relates to undercoats of nickel or palladium for rhodium deposits.

272. Baker & Co. Inc. *Fr.* 749,846 (1933); *Brit.* 413,342 (194).
The solution is prepared by reaction of a rhodium compound with phosphoric acid in sulphuric acid solution.

373. G. Grube & E. Kesting, *Z. Elektrochem.* **39**, 948-58 (1933).
Rhodium plating from sulphuric, fluosilicic, fluoboric, perchloric and oxalic acid solutions. The effect of excess free acid. C.D/potential curves are given.

274. F. Zimmermann & H. E. Zschiegner, *U.S.* 1,981,820.
A rhodium-phosphate compound in dilute sulphuric acid is used.

275. Baker & Co. Inc. *Ger.* 621,731 (1935).
Rhodium phosphate in phosphoric acid and/or sulphuric acid solution.

276. Baker & Co. Inc. *Brit.* 438,365 (1935).
Preparation of an ammino nitrite solution.

277. Baker & Co. Inc. *Fr.* 791,298 (1935).
Stripping rhodium deposits in phosphoric acid, acetic acid, hydrochloric acid, etc.

278. W. C. Heraeus, *Brit.* 440,938 (1936).
A solution of a boric acid compound of rhodium in the presence of sulphuric acid.

279. W. C. Heraeus, *Ger.* 627,264 (1936). *Fr.* 793,196-7.
Ranges of rhodium deposits from grey to black are obtained by addition of an organic colloid or colloid forming substance, *e.g.*, gelatin, starch or sugar.

280. F. Küch, *Metallwirtschaft* **15**, 569-70 (1936).
Methods of rhodium plating and its uses.

281. W. C. Heraeus, *Brit.* 446,393 (1936).
Dark deposits are obtained by adding sulphuric acid and a colloid, *e.g.*, gelatin, starch, benzyl alcohol, a benzoate, phenol or a phenolate.

282. S. Cohn, Baker & Co. Inc. *U.S.* 2,057,475 (1936).
Brilliant rhodium deposits from aqueous alkali solution containing rhodium combined with phosphoric acid. *U.S.* 2,057,476 relates to an aqueous solution containing a rhodium lactate.

283. K. SCHUMPELT, BAKER & CO. INC. *U.S.* 2,057,271 (1936).
Stripping composite nickel-rhodium coatings in phosphoric acid. *U.S.* 2,057,272 relates to a hydrochloric acid–sodium chloride–aluminium sulphate solution.

284. C. W. KEITEL, BAKER & CO. INC. *U.S.* 2,067,534 (1937).
A solution prepared by dissolving rhodium ammonium nitrite in 5% sulphuric acid.

285. F. ZIMMERMANN, BAKER & CO. INC. *U.S.* 2,067,747 (1937).
An alkaline electrolyte is prepared by dissolving an ammonium rhodium nitrite compound in ammonia.
U.S. 2,067,748 relates to a similar aqueous solution.

286. W. C. HERAEUS, *Ger.* 637,777 (1936).
Rhodium is precipitated by electrolysis of a solution containing rhodium borates or fluoborates, and sulphuric acid.

287. W. KEITEL. *Can.* 365,965 (1937).
A solution of a rhodium ammonium nitrite compound in 5% sulphuric acid gives very white deposits.

288. ÉTABLISSEMENTS MARRET, BONNIN, LEBEL & GUIEU, *Fr.* 803,273 (1936); *Ger.* 667,199 (1938).
Solution of hydrate or oxide of rhodium in nitric acid. Sulphuric acid and sodium sulphate may be added to increase conductivity.

289. W. J. WRIGHTON, *U.S.* 2,098,411 (1937).
Spectacle lens mountings etc., are plated with gold, rhodium and tin, and alloyed

290. E. A. OLLARD, *Met. Clean. & Fin.* **9**, 929-34 (1937).
Non-tarnishable finishes. Properties of chromium and rhodium deposits.

291. ÉTABLISSEMENTS MARRET, BONNIN, LEBEL & GUIEU, *Brit.* 480,145 (1938).
Solutions of oxides and hydrates of rhodium in nitric acid.

292. G. BUSS, *Mitt. Forsch. Inst. Probieramts Edelmetalle, Staatl, höheren Fachschule schwäb. Gmünd* **12**, 35-48 (1938).
Rhodium plating and deplating, its uses. Various solutions are given. A.C. is used for deplating.

293. E. RAUB & G. BUSS, *Z. Metallkunde* **30**, 152-7 (1938).
Stripping rhodium from nickel by A.C. treatment in hydrochloric acid.

294. R. W. HARBISON, *Deut. Goldschmiede Ztg.* **40**, 331-2 (1937); *Chem. Zentr.* 1938, I, 174.
Rhodium plating methods. Deposits over 25μ are dull. A platinum chloride–rhodium chloride–sodium nitrate solution is described for 90% platinum—10% rhodium deposits.

295. R. PIONTELLI & A. GIULOTTO, *Chimica e industria (Italy)* **21**, 478-9 (1939).
Plating from sulphamic acid solutions. Rhodium is one of the metals plated satisfactorily.

296. A. BREGMAN, *Iron Age,* **144**, 31-3 (*Nov.* 1939); *Met. Eng. Digest (Met. & Alloys)* **11**, *No.* 1, 32 (1940).
Composition and control of rhodium solutions. Physical properties of the deposit, etc.

297. R. Piontelli, *Chimica e industria (Italy)* **22**, 61-2 (1940).
The process of plating rhodium from sulphamic acid solution is described.

298. J. B. Kushner, *Met. & Alloys,* **11**, 137-140 (1940).
Modern rhodium plating. Physical properties of rhodium are described.

299. A. Spies, *Ger.* 692,122 (1940).
A sulphuric acid solution containing vanadium or uranium or complex platinum salts, fluosilicic acid or its salts. Di- or tri-methyl amines or ethyl amines give fine grained deposits. Tartaric, lactic, malic and maleic acid increase brightness.

300. E. Armstrong, *Met. Treatment,* **6**, 147-65 (1941)
Operating details of silver, silver-rhodium, gold and rhodium plating.

301. M. Weisberg, *Met. Fin.* **38**, 587-9 (1940), *No.* 12, 647-50, **39**, No. 1, (16-22 (1941).
Various rhodium baths are described in detail Experimental work on operating conditions.

302 Yūzō Yamamoto, *Tōkyōhurito Kōgyō-syorei kwan Kwagaku Kenkyu Hōkōka (Repts. Chem. Research Prefectural Inst. Advancement Ind. Tokyo) No.* 2, 2-12 (1940).
Influence of acid concentration, temperature, current density and rhodium content in sulphate and phosphate solutions, etc.

303. S. I. Orlova & N. P. Kolonina, *Korrozya i Borba s Nei, No.* 2, 32-6 (1940).
The sulphate and phosphate baths are compared. Current density, cathode efficiency, corrosion resistance and reflectivity are discussed.

304. E. H. Laister, *J. Electrodep. Tech. Soc.* **18**, 69-76 (1943).
Wartime applications of precious metal plating.

305. R. Piontelli, *Korrosion & Metallschutz* **19**, 110-3 (1943).
Excellent deposits of rhodium are obtained from sulphamic acid solution.

306. A. Brenner & W. A. Olson, *U.S.* 2,401,331.
Removal of metals which impair brightness, by addition of ferrocyanide.

307. J. J. Manley, *Proc. Phys. Soc. (London)* **57**, 136-44 (1945).
Rhodium plating standard weights.
See also: 215, 216, 218, 219, 225, 228, 229, 231, 232, 233, 234, 235, 236, 237, 240, 244, 245, 247, 248, 249, 250, 253, 254, 258, 260, 266, etc.

SECTION II.—ELECTROLYTIC POLISHING.

[A] METALLOGRAPHIC APPLICATION

(1) GENERAL AND MISCELLANEOUS.

308. P. A. Jacquet, *Compt. rend.* 201, 1473-5 (1935).
Polishing metals in 400 g/l. phosphoric acid.

309. P. A. Jacquet, *Soc. de Chim. Phys.* **33**, 226 (1936).
Micrographic study of effect of mechanical polishing on metal surfaces.

310. P. A. JACQUET, *Fr.* 202,403 (1936).

311. P. A. JACQUET, *Bull. Soc. Chim.* (5) **3**, 705-23; *Bull. Soc. France. Elec.* **6**, 547 (1936).
Copper, lead, tin and alloys are polished in phosphoric acid.

312. P. A. JACQUET, *Compt. rend.* **204**, 172-4 (1936).

Application to study of electrodeposits. (*ibid.* **204**, 1320 (1936).

313. W. C. ELMORE, *Phys. Rev.* **51**, 982 (1937), **53**, 933 (1938), **56**, 210 (1939).
Electropolishing and magnetic properties and structure of metal surfaces.

314. L. CAPDECOMME, *Research on the Measure of Reflecting Power by means of the Microscope. Thèse, Paris,* 1937.

315. P. A. JACQUET, *Electrodep. Tech. Soc.—Proc. 1st Intern. Conf. London,* 1937.
Comparison of mechanically and electrolytically polished surfaces.

316. P. A. JACQUET, *Journal Intern. de Chronometric et de Metrologie* (*Paris* 1937). *Proces verbaux et memoires,* 1939, 624.
Structure of mechanically and electrolytically polished surfaces.

317. P. A. JACQUET, *Entretiens. Scientifique de l'Acad. Medit.* (*Monaco* 1937); *Calvier* 1937, VI, 256.
Preparation of polished crystalline metallic surfaces.
Rév. Mét. **35**, 41, 116, 176 (1938).

318. P. A. JACQUET, *Métaux et Corrosion,* **13**, 86-91 (1938).

319. P. A. JACQUET, *Rév. Mét.* **35**, 41, 116, 176 (1938).
Structure of electrodeposits.

320. P. A. JACQUET, *La Technique Moderne* (*Aug.* 15, *Sept.* 21, 1939), **31**, 561,569.
Methods and applications of electropolishing.

321. R. B. GORDON & M. COHEN, *Am. Soc. Met Preprint* **39** (1939).

322. G. KUHN, *Met. Progress,* **36**, 755 (1939).
"Speedy polishing without abrasives."

323. C. SCHAEFER, *Met. Industry* (*N.Y.*) **38**, 22-6 (1940).
The anodic polishing of copper, brass, bronze, iron, steel, tin, lead, nickel, zinc and cobalt.

324. H. R. NELSON, *Phys. Rev.* **57**, 553 (1940, March).
Electron diffraction experiments on electropolished surfaces.

325. L. CAPDECOMME, *Bull. Soc. France. Mineralogie,* **64**, 160 (1941).
Optical characteristics of metallic crystals.

326. L. CAPDECOMME & M. ORLIAC, *Compt. rend.* **213**, 333-5 (1941); *Met. Abs.* (*in J. Inst. Met.*) **9**, 71, 1942.
25% potassium hydroxide or 10% perchloric acid (d. 1·479) in acetic acid solutions.

327. E. KNUTH, A. L. DE SY & H. HAEMERS *Stahl und Eisen* (*Feb.* 20, 1941), 185, *ibid,* **61**, 777-8 (1941).
Perchloric acid, and ferric chloride-nitric acid solutions for polishing stainless steel and other metals.

328. E. HUGONY. *Met. ital.* **33**, 343-8 (1941). *Chem. Zentr.* 1942, I. 2321.
A perchloric acid solution for polishing steel, aluminium, lead and tin.

329. L. CAPDECOMME, *Métaux-Corrosion-Usure,* **16**, 77 (Oct. 1941).
Metallographic study of polished metal surfaces.

330. N. N. POSOKHIN, *Zavodskaya Lab.* **10**, 398-400 (1941); *Chem. Zentr.* 1943, I. 186.
Details of methods for copper, brass, aluminium, iron, steels, etc.

331. O. E. BROWN & C. N. JIMISON, *Met. Progr.* **40**, 298 (1941); *Met. Ind.* **59**, 326 (*Nov.* 21, 1941).
"An improved cell for electropolishing."

332. *Am. Soc. Testing Materials, Standards,* E3-42T, *Vol.* 1 (1941).

333. F. KELLER, *Iron Age,* **147**, 23 (*Jan.* 9, 1941).
Polishing metals for micrographic examination.

334. L. v. HÁMOS, *Jernkontorets. Ann.* **126**, 568-90 (1942).
Apparatus and procedure for polishing steels for X-ray analysis, also stainless steel, copper, brass, aluminium and white metal.

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Application to study of the crystallographic properties of zinc, tin, aluminium and copper.

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(4) IRON AND STEEL.

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Application of electropolishing to ferrous metals.

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"A simplified method for polishing steels."

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[B] INDUSTRIAL APPLICATION.

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A chromic acid solution for electropolishing.

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Satin and polished finishes obtained with two hydrofluoric acid-sulphuric acid solutions on stainless steel, etc.

394. Brevets Aero Mecaniques Soc. Anon. *Fr.* 850,135 (1939); *Brit.* 524,272 (1940).
Phosphoric acid solutions for polishing metals.

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Stainless steel, copper, brass, nickel, aluminium and monel metal are polished. The results and the theory of electropolishing are discussed.

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Metals are polished in phosphoric acid-sulphuric acid solutions.

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Electrolytic cleaning, pickling and polishing.

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Iron, cobalt, nickel and chromium are polished in an electrolyte containing ions lower than the sulphate ion in Cooper's lyotropic table (C. A 31,2900^{9}) and capable of forming easily soluble salts with the metal.

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Polishing methods for steels, alloy steels, aluminium and aluminium alloys.

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Cadmium, zinc and silver are polished in 5% potassium cyanide.

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Theory and methods for copper, zinc, tin, aluminium, nickel, cobalt, iron and alloys.

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A sulphuric acid–glycerol solution for polishing German silver, iron, nickel and alloys.

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Phosphoric acid is preferred to sulphuric acid. A better finish is obtained and smaller voltages are required. References.

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Arsenic acid with one or more mineral acids for polishing metals. See also *U.S.* 2,282,351.

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Recent investigations.

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Mechanical and electrolytic polishing and cleaning before plating.

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Electropolished nickel, copper and stainless steel is given a flash deposit before bright (chromium etc.) plating to overcome cloudiness In case of nickel, a flash deposit of 0·00005″ nickel is given from a modified Watts solution at *p*H 1·0, containing a wetting agent.

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Production scale processes for steels, stainless steel, copper, brass, aluminium, monel metal, etc.

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Review of preplating processes including electropolishing.

Procedures, their uses and limitations.
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Solutions of (*a*) low—and (*b*) high electrical resistance are described. (*a*) phosphoric acid with acetic acid, sulphuric acid, chromic acid, etc. (*b*) perchloric acid with acetic acid, alcohol, ether. 57 solutions for aluminium, copper nickel, lead, tin, tungsten, zinc, brass and steel. Mainly stainless steel. 114 references.

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Mechanism of electropolishing, its applications and uses.

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Anodic removal of metal from surface, removed from solution at intervals for abrasive treatment.

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Mechanism of electropolishing. Irregularities in the case of viscous anodic layers.

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Application of electropolishing in Italy.

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434. C. L. Faust, *Proc. Am. Electroplat. Soc.* 1946, 49-73.
Historical survey and discussion of processes for all metals.

435. L. Ya Popilov, *U.S.S.R.* 66,401 (1946).
Apparatus using a mercury layer at bottom of tank as one electrode.

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Processes are described. Costs are given.

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Discussion of commercial applications.

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Fluosulphonic acid is used for polishing steel, alloy steels and non-ferrous metals.

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Phosphoric acid-glycerol solution for stainless steel, nickel, brass, etc.

440. R. E. HALUT, *3rd Intern. Conf. on Electrodeposition* (*London*, 1947), *No.* 2.
Industrial applications of electropolishing.

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(2) NICKEL.

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Nickel plated articles are polished anodically in sulphuric acid. (*See* 442).

442. E. E. LINDH, *U.S.* 2,145,518 (1939).
Sulphuric acid solution for nickel and nickel plated articles (*see* 441).

443. H. R. PRISTON, A. W. HOTHERSALL & R. A. F. HAMMOND. *Brit.* 504,026 (1939).
Sulphuric acid and addition agents comprising glycerol, nitric acid, sulphonates and chromic acid.

444. HOTHERSALLL & HAMMOND, *J. Electrodep. Tech. Soc.* **16**, 83-98 (1940).
Electropolishing of electroplated nickel v bright plating.

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The anodic polishing of nickel in sulphuric acid.

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Rejuvenating electrolytic nickel polishing solutions.

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A sulphuric acid–phosphoric acid–water solution for nickel, iron, their alloys and German silver.

449. S. WERNICK, *Automobile Eng.* **33**, 549-50 (1943).
Polishing nickel, stainless steel and aluminium.

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A phosphoric acid–sulphuric acid solution containing Al^{+3} and Cr^{+3}.

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Phosphoric acid–chromic acid–water solution for polishing nickel.

452. V. I. Lainer, *J. Appl. Chem.* (*U.S.S.R.*) **18**, 236-45 (1945).
Nickel is polished in sulphuric acid. The effect of the chloride ion is discussed.
(*See also*: 395, 397, 399, 400, 402, 410, 411, 412, 413, 419, 420, 422, 424, 428, 429, 434, 436, 437, 439, 440, etc.

(3) STAINLESS STEEL AND IRON.

453. R. W. Burns, & C. W. Warner, *U.S.* 1,658,222.
Phosphoric acid at 100 amp/sq. ft. and 122°F.

454. G. Kiefer, *Iron Age*, **144**, 30-2, 66-7 (*Dec.* 21, 1939).
Production scale processes for polishing stainless steel.

455. H. Burkhardt, *Ger.* 682,284 (1939).
Inorganic compounds able to dissolve steel, and organic compounds, *e.g.*, glycerol, tallow, benzoic or picric acid or inhibitors.

456. N. E. Promisel, *Mon. Rev. Am. Electroplat. Soc.* **27**, 423-8 (1940).
18–8 nickel–chrome steel, especially wire shelving, is polished in phosphoric acid, phosphoric acid–sulphuric acid or hydrofluoric acid solution.

457. H. H. Uhlig, *Trans. Electrochem. Soc.* **78**, 8 *pp.* (*preprint*) 1940.
A glycerol–phosphoric acid solution. Results are obtained expressed by readings from the photoelectric reflectometer. (*See* 404).

458. J. W. Lippert, *Iron Age* **145**, 22-6 (*Jan.* 1940).
" Pickle-polished stainless steel."

459. A. L. Field & I. C. Clingan, *Steel* **106**, *No.* 17, 54-6, 64 (1940).
An aqueous citric acid–sulphuric acid solution.

460. Alloy Research Corp. *Brit.* 529,944 (1940).
A water soluble organic acid, the stainless steel or iron salts of which permit ready flow of corrosion products away from anode, as well as a soluble sulphate compound, *e.g.*, citric acid–sulphuric acid solution.

461. E. Bergman, P. Erikson, G. Hildebrand & G. Frey, *Fr.* 852,312, *Brit.* 530,041.
Nitric acid solution at 700 amp/sq. ft. and 30°F.—160°F.

462. H. H. Uhlig, *Proc. Am. Electroplat. Soc.* 1941, 20-4 (*See* 457).

463. H. H. Uhlig, *U.S.* 2,172,421.
Hydrochloric acid–sulphuric acid–nitric acid solution containing titanium, at 160°—175°F.

464. C. L. Faust & H. A. H. Pray, *Steel*, **109**, *No.* 20, 80-2, 101-2 (1941).
The phosphoric acid–sulphuric acid solution is discussed.
Also in:

465. *Proc. Am. Electroplat. Soc.* 1941, 104-12.

466. J. Ostrofsky, *U.S.* 2,331,721 (1943).
A water soluble organic acid, *e.g.*, citric or tartaric, less than 10% methyl alcohol or other alcohols containing <6 carbon atoms.

467. C. L. Faust, *U.S.* 2,334,699. (*See* 448).

468. J. Ostrofsky, *U.S.* 2,335,354 (1943).
An aliphatic acid (*e.g.*, citric or tartaric acid)–sulphuric acid–water solution.

469. I. C. Clingan, *Can.* 422,922 (1944).
Chromium-nickel steels and iron are polished in sulphuric acid.

470. S. Wernick, *Steel* **115**, *No.* 24, 146-8, 176-80 (1944).
Practical suggestions on polishing 18–8 stainless steels.

471. G. J. Beckwith, *U.S.* 2,348,517 (1944).
An aqueous solution of glycerine–phosphoric–sulphuric acid.

472. G. J. Beckwith, *U.S.* 2,349,843 (1944).
A phosphoric–sulphuric acid-fluorescein–alcohol solution.

473. N. S. Mott, *U.S.* 2,357,219.
Nitric acid–hydrofluoric acid–hydrochloric acid solution at 180°—200°F.

474. C. L. Faust, *U.S.* 2,366,712 (1945).
A phosphoric acid–chromic acid–water solution.

475. Anon. *Iron Age* (*July* 12, 1945), 64.

476. Anon. *Steel* (*Sept.* 10, 1945), 104.

477. F. E. Drummond & D. E. Bench, *U.S.* 2,378,602 (1945), *Can.* 409,482.
Moulded stainless steel strip is polished in the apparatus described, using ferric sulphate–hydrofluoric acid, and other solutions. These include a saturated solution of sodium dichromate in sulphuric acid containing 5–25% of a high molecular weight, sulphonated alcohol of formula $CH_3(CH_2)_n\ OSO_3\ Na$ (where $n>10$), *e.g.*, cetyl or stearyl alcohol. Or a saturated solution of potassium dichromate in sulphuric acid containing 5% phosphoric acid.

478. I. C. Clingan, *U.S.* 2,379,006 (1945).
An aqueous sulphuric acid solution.

479. C. R. Hornwedel & W. J. Resch, *U.S.* 2,381,167 (1945).
A chromic acid–water–acetic acid–formic acid solution.

480. G. J. Beckwith, *U.S.* 2,411,410 (1946).
Addition of an inhibitor, *e.g.*, pyridine or a derivative, to sulphuric acid–phosphoric acid solutions.

481. C. Batcheller, *U.S.* 2,409,097 (1946).
Sulphuric acid and chromic, vanadic, metavanadic, manganic or permanganic acid and water.

482. I. Whitehouse & V. S. Chambers, U.S. 2,412,186 (1946).
Polishing the interiors of stainless steel tubes.

See also: 392, 393, 395, 396, 399, 404, 406, 411, 414, 418, 420, 421, 423, 424, 426, 428, 431, 434, 436, 437, 438, 439, 440, 449, etc. Also *U.S.* 2,424,674 (1947).

(4) ALUMINIUM AND ALUMINIUM ALLOYS.

483. R. B. Mason, *U.S.* 2,108,604.
A fluoborate solution.

484. J. M. Guthrie, *U.S.* 2,153,060.
A fluoboric acid solution.

485. R. B. Mason, *Brit.* 433,484.
Fluoboric acid (acetic acid+boron trifluoride).

486. R. B. Mason & M. Tosterud *Can.* 354,510 (1935) and *U.S.* 2,040,617 (1936).
A chromic acid–hydrofluoric acid solution.
Can. 354,511 and *U.S.* 2,040,618.
A sulphuric acid–hydrofluoric acid solution.

487. N. D. Pullen, *J. Inst. Met. Advance Copy* No. 744, 8 *pp.* (1936).
Dual process for polishing reflectors in (1) sodium carbonate–trisodium phosphate solution; (2) sodium bisulphate solution.

488. G. Kraft & N. L. Soloman, *Can.* 432,347.
Hydrofluosilicic acid.

489. M. Tosterud, *Can.* 423,091.
Phosphoric acid–glycerine solution.

490. O. L. Shawcross, *Can.* 423,093.
Phosphoric acid–glycol solution.

491. M. Guthrie, *Ger.* 675,273.
A chromate–carbonate solution.

492. C. H. R. Gower & E. Windsor-Bowen, *Brit.* 447,420.
A sulphuric acid–phosphoric acid–acetic acid–boric acid solution.
Brit. 447,421. A sulphuric acid–gallic acid–boric acid solution.

493. Tré Fileries et Laminoirs du Havre, *Fr.* 798,721.
A sulphuric acid–phosphoric acid–nitric acid solution.

494. M. Schor, *City Coll. Vector.* (*N.Y.*) **3**, 63-4 (1940).
Experiments on polishing aluminium.

495. Comp. Prod. Chim. Electromet. *Brit.* 521,290 (1940).
Sodium hydroxide or sodium sulphide, either alone or with a neutral salt of an alkali metal.

496. K. Hauffe & R. Tillig, *Metallwirtschaft*, **20**, 994-9 (1941).
Jacquet's and De Sy & Haemers' methods were studied. The perchloric acid–ethyl alcohol solution was also used on magnesium alloys.

497. A. Ensor, *J. Electrodep. Tech Soc.* **18**, 13-20 (1942).
The Brytal process for the anodic oxidation of aluminium.

498. G. Elssner, *Ger.* 743,194 (1943).
Aluminium and aluminium alloys are polished in alkali triphosphate solutions containing salts the anions of which loosen the dense anodic layer and have a solvent action on the extraneous deposit.

499. N. D. Pullen, *U.S.* 2,339,806 (1944).
A sodium carbonate solution containing an ammonium salt with or without phosphates, etc.

500. M. Tosterud, *U.S.* 2,375,394 (1945).
Aluminium castings containing 5% silicon are polished in hydrofluoric acid–glycerol–water solution.

See also: 395, 408, 410, 411, 418, 421, 422, 425, 434, 436, 437, 440, 448, etc.

(5) IRON AND STEEL.

501. C. P. Madsen, *U.S.* 1,562,710 (1925).

502. N. R. Laban, *J. Electrodep. Tech. Soc.* (1930), **5**, 128.

503. G. B. Hogaboom, *U.S.* 1,865,472.
Electrolytic bright dipping.

504. C. W. Yeger & G. Todd, *U.S.* 2,165,326 (1939).
Apparatus for pickling and bright dipping ferrous metals anodically.

505. C. B. F. Young & W. L. Brytozuk, *Met. Fin.* **40**, 237-41, 306-12, 317 (1942).
Optimum conditions are found by photoelectric reflectometer. For commercial work, phosphoric acid–sulphuric acid solutions gave surfaces of 60% reflection. For metallographic specimens, acetic anhydride–perchloric acid solution is best.

506. R. P. Delaplace & C. Béchard, *U.S.* 2,294,227 (1944).
Pyrophosphoric acid in a non-aqueous solvent, *e.g.*, ethyl alcohol.

507. C. L. Faust, *U.S.* 2,338,321 (1944).
Plain low-carbon or low-alloy steels are polished in phosphoric acid–chromic acid–sulphuric acid solution.

508. C. L. Faust, *U.S.* 2,347,040 (1944).
Steels are polished in phosphoric acid–chromic acid–water solution.

509. W. A. Sparks, *J. Electrodep. Tech. Soc.* **21**, 245-64 (1947).
carbon–and manganese steels are polished in sulphuric acid–phosphoric acid solution.

See also: 392, 393, 395, 397, 398, 399, 400, 406, 408, 410, 411, 412, 418, 419, 421, 424, 427, 428, 431, 434, 436, 437, 438, 440, 448, etc.

(6) COPPER AND COPPER ALLOYS.

510. Fr. Le Matériel Telephonique. *Fr.* 707,526 (1931).
Phosphoric acid 70%, ether 30%. Also acetic acid–perchloric acid solutions and phosphoric acid–alcohol solutions.

511. P. A. Jacquet, *Swiss*, 187,439.
Copper is polished in phosphoric acid at 100—1000 amps/sq. ft. and 60—120°F.

512. C. Benedicks & B. Ljunggren, *Arkiv. Kemi. Mineral Geol.* **13A**, No. 25, 14 *pp.* (*preprint*) (1940).
A phosphoric acid solution for polishing copper.

513. R. Manuel, *U.S.* 2,330,170 (1943).
Zinc, copper, and their alloys are polished in water–chromic acid–sodium dichromate–sulphuric acid–acetic acid solution.

514. J. L. Rodda, *Mining & Metall. Vol.* 24, *July* 1943, *p.* 323.
Polishing zinc and brass in 200 g/l chromic acid at 2000 a/ft.^{2}.

515. C. L. Faust, *U.S.* 2,347,039 (1943).
A phosphoric acid–chromic acid–water solution for copper.

516. C. L. Faust, *U.S.* 2,366,714 (1945).
A phosphoric acid solution containing trivalent aluminium and chromium for polishing copper.

517. C. L. **Faust**, *U.S.* 2,407,543 (1946).
Brass is polished in phosphoric acid–chromic acid–water solution.

518. P. **Berger**, *3rd Intern. Conf. on Electrodeposition (London,* 1947), No. 4.
Electropolishing of brass pressings. Description of new processes.

See also: 395, 397, 399, 407, 410, 411, 414, 415, 418, 420, 421, 422, 423, 424, 425, 428, 430, 433, 434, 437, 439, 440, etc.

(7) SILVER.

519. E. **Spitalsky**, *Ger.* 225,873.
Silver is polished at 7 amps/sq. ft. and room temperature.

520. L. I. **Gilbertson** & O. M. **Fortner**, *Trans. Electrochem. Soc.* **81**, 10 *pp.* (*preprint*) (1942).
Anodic polishing of silver in cyanide silver solution.

521. **Anon.** *Iron Age, June* 6, 1945, 65.
New method for polishing silver plate.

522. **Anon.** *Iron Age, August* 1946, 49.
Electropolishing of silver.

523. D. **Gray** & S. E. **Eaton**, *Iron Age*, **159**, *No.* 15, 64-5 (1947).
Polishing silver in a silver cyanide solution containing potassium cyanide and potassium carbonate.
Also *U.S.* 2,416,294.

See also: 409, 411, 431, 440, etc.

(8) ZINC

524. H. **Strecker**, *Ger.* 302,902.
Zinc is polished in 50° Bé zinc chloride solution at 60°F.

525. C. L. **Faust**, *U.S.* 2,373,466 (1945).
Zinc and its alloys are polished in a phosphoric acid–water–chromic acid solution.

526. C. H. **Ward**, *U.S.* 2,399,964 (1945).
A process of plating in acid zinc solution and subsequent electropolishing.

See also: 409, 410, 411, 418, 424, etc.

(9) CADMIUM.

527. J. **Liger**, *Bull. Soc. Chim.* **4**, 568-72 (1944).
A potassium cyanide solution containing $K_2Cd(CN)_4$ is used for polishing cadmium.

See also: 404, 411, etc.

(10) LEAD.

528. L. **Koch** & H. **Staunau**, *Metallwirtschaft*, **20**, 752-5 (1941).
A perchloric acid–acetic anhydride solution for polishing lead.

See also: 411, 424, etc.

(11) GOLD.

529. J. B. **Kushner**, *Prod. Fin.* **7**, *No.* 2, 42-4 (1942).
The electropolishing of gold is described.

See 400, 424.

(12) TIN, CHROMIUM AND COBALT.

See 400, 424.

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[*Note:* Numbers printed in italics refer to reference numbers in the bibliography.]

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