The investigation of electroplating

and related solutions with the aid of

THE HULL CELL

by Walter Nohse

with the collaboration of Josef Heyes and Gunter Wagenblast

translated from the German and edited by

the Staff of Electroplating and Metal Finishing

with additional information by R. O. Hull & Co. Inc., Cleveland, Ohio

PUBLISHER'S NOTE

IN RECENT years the Hull cell has come to be recognised as a most important tool in the control testing of electroplating and related solutions. The apparatus required is simple and inexpensive, the test takes only a few minutes to perform and does not require a particularly skilled operator. Yet with its aid much can be learnt about the composition and characteristics of a plating solution ; a chromium plating bath, for example, can be controlled and maintained by using only a hydrometer and a Hull cell. The hydrometer checks on the chromic acid while the Hull cell determines the catalyst ratio and impurity level. The Hull cell thus provides an extremely valuable plating control test.

What it does require however is skilled interpretation of the test panels obtained, comparisons being made with panels plated in solutions of known composition and purity and under known conditions. In the course of time most users of the Hull cell will accumulate a considerable amount of comparative data. For the newcomer however the problem is how to establish the large number of necessary standards of comparison for which ideally one should take each plating solution in use and investigate the effects of altering each and every parameter—major and minor constituents, impurities and operating conditions—in small steps both singly and in combination.

This is where this book is of value because the Authors have themselves carried out these investigations and produced many hundreds of test panels from which nearly 200 have been selected and are reproduced in these pages for use by the operator in the interpretation of his own test results. Detailed written information on the Hull cell behaviour of plating solutions in various conditions of balance and under various plating conditions is also included together with notes on the use of the Hull cell for investigating covering power, current and metal distribution, metal surface condition, anodic processes including electropolishing and the suitability of tank linings.

This book was first published in Germany by the Eugen G. Leutze Verlag, Saulgau/Württ., in 1956 and a second edition was published in 1965. The English translation was made by members of the staff of *Electroplating and Metal Finishing* who also edited the manuscript and included much additional information on the design and use of the Hull cell. Chapters 1 and 2 have in fact been completely re-written. We should like to express our thanks to R. O. Hull & Co. Inc. for their co-operation in providing this additional information together with the whole of Chapter 9, and in particular to Dr. M. M. Beckwith, Vice-President, who also checked through the whole manuscript, for his most helpful comments and suggestions.

Teddington, June 1966

PREFACE TO THE FIRST GERMAN EDITION

THE IDEA of this book followed my own endeavours to form a photographic file of Hull cell panels illustrating various phenomena which arise in using the cell. Only during the course of this work did it occur to me that a collection of photographs of this type in book form would be of great help to others who use the Hull cell for testing solutions, and not least to the untrained apprentice. The basic material for this volume was therefore formed by many illustrations which I believe are capable of describing the appearance of Hull cell panels much better than the most comprehensive verbal descriptions. The reader who studies the illustrations and the accompanying text will save himself much effort in his attempts to interpret and evaluate the panels.

One problem which presented itself in reproducing the appearance of the panels photographically was how to show lustre and brightness. There appeared to be three ways of doing this. I could let the panel reflect a white light source. This showed fully bright surfaces as white and without structure while the less bright and matt surfaces appeared grey due to their lower specular reflectivity. If on the other hand the bright parts of a surface reflected a black colour, they would appear as black and without structural features. In this case again, the matt parts of the surface appeared grey due to the fact that they reflected diffuse light. I found that black gave a better contrast against less black surfaces than white against less white ones. For this reason I decided to use black reflections. This is also justified by the fact that a considerably larger number of areas would appear as light than as dark corresponding to bright and matt areas of surfaces. The third possibility, that of choosing a black-and-white pattern for the reflection source, was eliminated as giving rise to too much distortion and also because the pattern would mask structural features of the panels.

In order that this book should not be too long, I have restricted it to the most important plating solutions used in practice. My thanks are due to the Eugen G. Leuze Verlag for their careful attention to the compilation of the illustrations.

Bielefeld, June 1956   WALTER NOHSE

PREFACE TO THE SECOND GERMAN EDITION

SINCE THE publication of this book in 1956 the Hull cell has established itself widely both in the laboratory and in the factory. The need for a second edition, which finds its reason in the rapid sales of the original edition, demonstrates that today the Hull cell has become a standard method of control in the electroplating shop.

July 1962 saw the appearance of the German Standard DIN 50 957 which laid down the principles of the use of the Hull cell for testing electroplating solutions. In the meantime two different cells with capacities of 250 and 1000 ml respectively have come into use ; of these the 250 ml cell is the most frequently employed.

In describing the Hull cell and its method of operation, I have made good use of the information in DIN 50 957 and where it seemed necessary I have amplified this for the practical plater. The abbreviations for 'porous', 'rough' and 'no deposit' have been altered although their visual symbols remain almost unchanged.

In the second edition, further work has been added which is designed to show the versatility of the Hull cell. The last two chapters in this edition consist of a chapter written in collaboration with Ing. G. Wagenblast on the investigation of nickel plating salts in the Hull cell and a section contributed by Dr. J. Heyes on the measurement of metal distribution in electroplating solutions.

My gratitude for support in further experiments and for many helpful suggestions is due to Mr. Richard Hull Jr., Mr. Günter Wagenblast and Dr. J. Heyes.

Lippstadt/Westf, Spring 1965   WALTER NOHSE

CONTENTS

CHAPTER 1

THE HULL CELL

Why use a Hull cell?

A PLATING bath is a solution of a number of chemicals each of which has a certain effect on the properties of the electrodeposited metal coating. In order, therefore, to obtain electroplated coatings of the desired properties it is necessary to know the composition of the electrolyte. In as far as this concerns the concentrations of metal and other salts, there are a sufficient number of analytical methods known today which, with the aid of simple techniques, a little experience and care in operation, give results of sufficient accuracy.*

However, such methods of analysis are sometimes time-consuming, for instance, the determination of catalyst concentration in chromium plating solutions. Moreover they are not generally suited to the control of organic addition agents. Although the type of compound employed for this purpose is often known from the patent literature, it is rare that the plater knows the exact chemical composition and it is seldom that analytical methods are available to him for determining the concentration in the plating solution. From the practical point of view this is dangerous because a small departure from the optimum concentration of such addition agents will not normally produce any visible change in the electrodeposit produced under the normal

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* 'The Analysis of Electroplating and Related Solutions' by K. E. Langford, Robert Draper Ltd., Teddington.
'Schnellanalysenmethoden für galvanische Bäder' by R. Weiner and C. Schiele, Eugen G. Leuze Verlag, Germany.

plating conditions and it is impossible for the plater to obtain advance warning in this way of a dangerous deterioration in the solution. Fortunately however changes are more easily visible in deposits produced under other conditions of electrodeposition and the Hull cell is a very suitable tool for such plating tests.

It was first described by R. O. Hull in a paper entitled 'Current density characteristics, their determination and application' (*Proc. Amer. Electroplaters' Soc.*, 1939, **27**, 52 - 60) and its application in the electroplating industry has been well summarised by Armet* in the following words. "The Hull cell may be employed usefully for the control of most types of plating solutions. One of its great advantages is the fact that it is possible for the skilled worker to assess the deposit characteristics at varying current densities all on one test panel. It is furthermore possible to carry out tests at various temperatures and current densities, and so to get a good idea of the bath characteristics and of the changes due to the variables introduced.

"The following effects may be investigated using the Hull cell.

1. Variation in main solution constituents and addition agents.
2. Operational variations such as temperature and current density.
3. Effect of organic and/or metallic contamination of the solution.
4. Investigations of tank linings, i.e. rubber and plastics, which might be suspect. Hull cell panels may be conveniently stored in the desiccator, or in plastic envelopes as permanent records of solution characteristics.

"It is possible with regular Hull cell tests to anticipate plating solution faults well in advance of their becoming a production danger. This is because of the fact that it is possible to see results at current densities both higher and lower than those obtained in production working, and it is normally in these areas that troubles first manifest themselves. Such troubles, though very apparent over a range of laboratory plating tests, quickly extend to the production plating if not rectified.

"It is a fairly well established fact that all plating baths, even of the same solution, are individual and distinct from each other. When complex impurities accumulate, it is often very difficult to control such solutions as chromium plating solutions, by chemical analysis alone, and in cases such as this the Hull cell proves invaluable.

"In cases where chemical analysis points to the need for large additions to be made to a solution, the Hull cell test can be used to check whether it is safe to make such additions in one go without upsetting the bath equilibrium. The Hull cell test can demonstrate the presence of plating solution impurities in quantities so small as to be difficult to detect chemically but which can

* R. C. Armet. 'Electroplating Laboratory Manual', Robt. Draper Ltd., Teddington

nevertheless cause production difficulties. A very good example of this is the detection of chlorides in chromium plating solutions, which will cause a deterioration in covering power."

However, while chemical analysis yields quantitative results, a Hull cell test only presents the investigator with a picture, and in order to interpret the picture, standards are required for comparison. Such standard pictures have not, to the Author's knowledge, been published before and it is the aim of this book to present illustrations demonstrating the effects on the Hull cell deposit of changes in the main constituents of the more important electroplating solutions and thereby to save the reader the task of carrying out his own experiments.

Hull cell design

The Hull cell is a miniature plating vat having a particular trapezoidal plan (see Fig. 1 *et seq*). The shape and dimensions are most important as
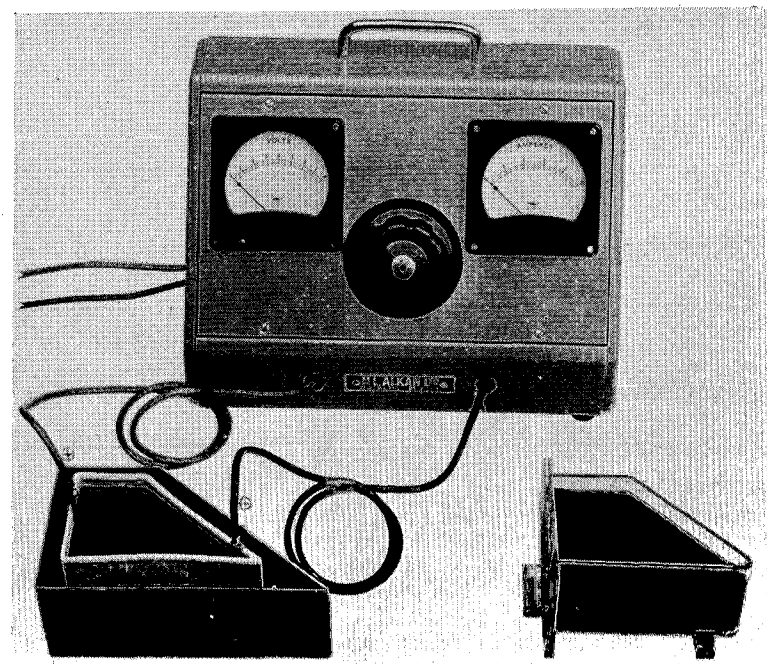

Fig. 1. Commercial (British) Hull cell apparatus showing the cell, water bath and current control panel.   [*Courtesy M. L. Alkan Ltd.*
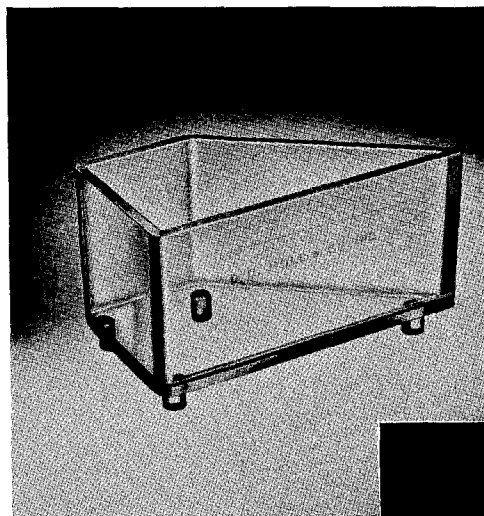
Fig. 2. 267 ml Hull cell. The 250 ml and 320 ml cells differ only in the depth of solution employed.

Fig. 3. 534 ml Hull cell recommended for extended testing because of the relatively smaller change in bath composition and temperature during a series of tests.
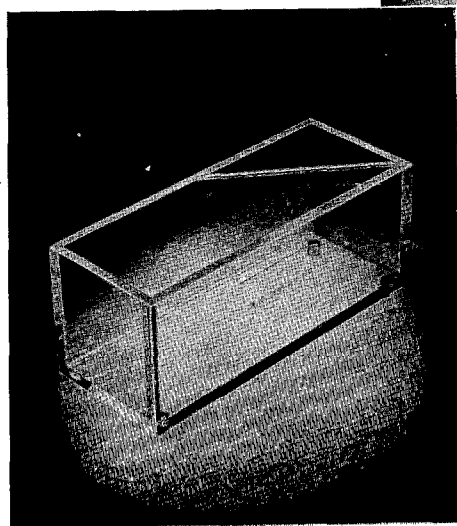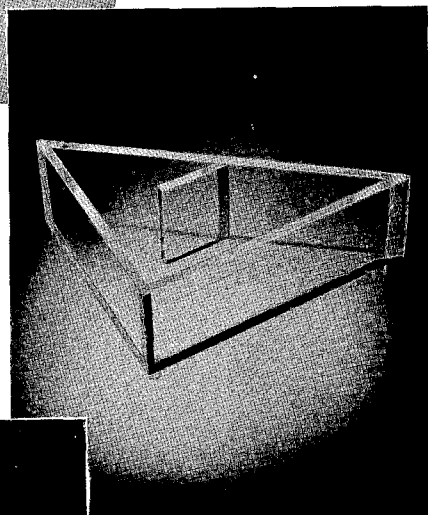

Fig. 4. 1000 ml Hull cell.

will be seen below. It is manufactured in various sizes, 250, 267, 320, 534 and 1000 ml, mainly for operating convenience. The intending user would buy either the cell itself and make his own arrangements for current supply, etc., or a complete test apparatus with current supply, control panel and water bath (or immersion heater) as shown in Fig. 1.

The original cell upon which Dr. Hull's calculations were made was the 1000 ml cell but while it proved quite successful in practice, it was felt that a smaller capacity cell might prove more convenient to use. So the 267 ml cell was developed, this capacity being chosen to assist in the rapid calculation of required additions to the plating bath since 2·0 g of any addition per 267 ml are equivalent to 1·0 oz per U.S. gallon. For the same reason the 320 ml cell was developed for use in Britain (2·0 g of additive per 320 ml are equivalent to 1·0 oz per Imperial gallon) while the 250 ml cell is popular on the Continent of Europe.

However, these small Hull cells have been criticised for being too small in that solution composition and temperature can change rapidly in spite of precautions and the designers now recommend the 534 ml cell which is not only double the volume but also of a different shape, allowing alternative test procedures. The increased volume allows more tests to be conducted before the condition of the solution changes sufficiently to nullify the results. Generally, on a bright nickel plating bath, the maximum number of tests recommended (without any correction of the solution for pH) in the 267 ml cell is three and in the 534 cell five. Temperature control is also better. Frequently, tests are run for 5 min at 25 to 30°C with cathode currents of 1 to 3 amps and in practice the temperature of the 534 ml bath does not appreciably increase under these conditions. Also if the anode for the system being tested has a relatively low polarizing current density, then the 534 is preferable because two or three anodes can be used with a single cathode thus bringing the anode current density below the limiting value. The 534 Hull cell uses the same size panel and the same current density scale as the 267.

People who use the 1000 ml cell generally do so because they prefer the even smaller temperature rise which results from the passage of a given amount of current. Also, a larger cathode is employed on which it is easier to detect minute effects occurring in the test bath. This larger panel is also used in the Hanging Hull Cell to which reference will be made later.

In the Hull cell the cathode is fixed at an angle to the anode and, in most models, both anode and cathode occupy the full cross section of the cell. The shape and actual dimension of the cell are most important in determining the cell current distribution; the cathode angle of inclination was arrived at only after careful thought and research and, if this is changed, current distribution will no longer remain independent of the nature of the electrolyte.
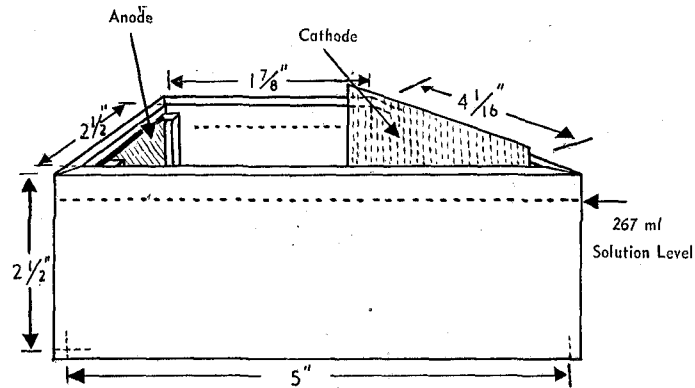
Fig. 5. 267 ml capacity Hull cell. All measurements given are internal and in inches. The 250 ml and 320 ml cells have the same plan measurements but the solution level is lowered and raised respectively to yield the appropriate capacity.
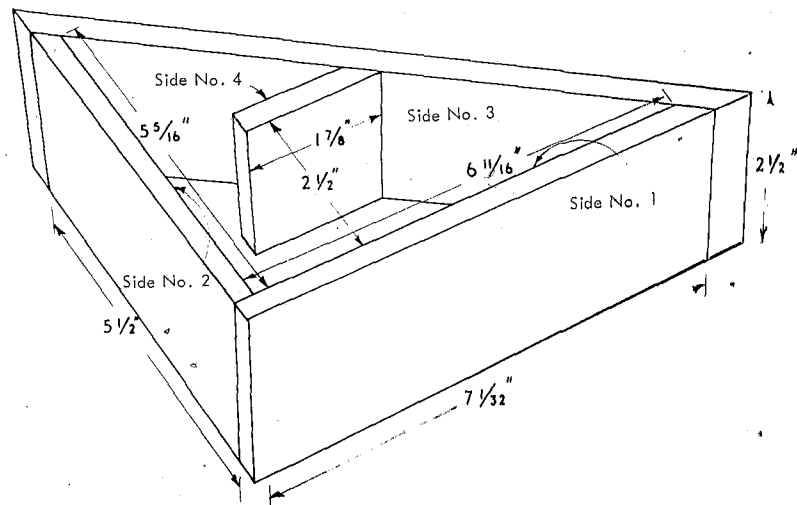

Fig. 6. 534 ml Hull cell. All measurements given are internal and in inches.
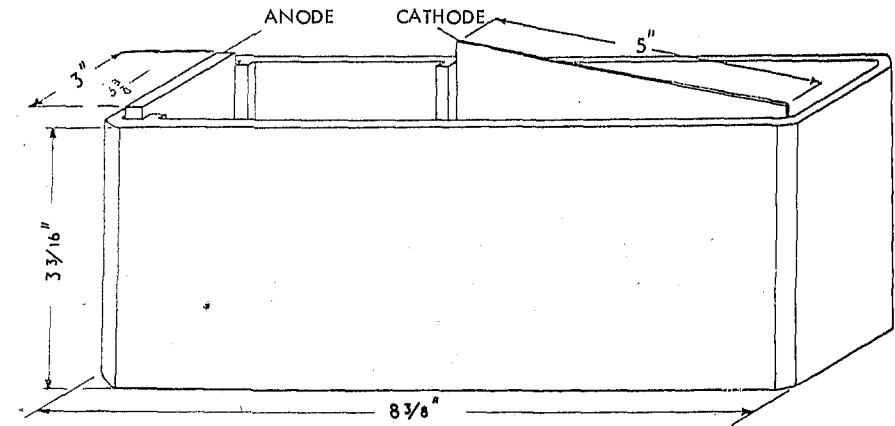
Fig. 7. Dimensions of the 1000 ml Hull cell.

The various cells, their dimensions and test lay-outs are shown in the illustrations. The 250, 267 and 320 ml cells are identical except in regard to the depth of electrolyte employed and, of course, to the relation between the applied cell current and the scales or printed curves relating distance to primary current density (see Chapter 2).

Hull cells are manufactured under one or more of the following U.S. Patents: 2,149,344 ; 2,760,928 ; 2,801,963 ; 3,121,053.

Material of construction

The cell must be manufactured from a non-conducting material which is also completely inert to the electrolyte being tested. As the Hull cell is frequently used to test for impurities in solution, this latter requirement is most important. Perspex is the most usual material of construction and is suitable for all plating solutions other than chromium. Its transparency is an advantage in that one can see better what is happening to the cathode during the test and also that one can see the back of the cathode, which is close to the cell wall. Polythene is also used and PVC and PVC-lined steel are sometimes encountered. A new development by the R. O. Hull & Co. Inc. is a moulded polypropylene cell for chromium plating solutions which is preferable to the porcelain enamelled iron cell previously recommended.

Since stability of size and shape are important even when hot solutions are being tested, the plastic material must be carefully joined with adhesive or by welding. One piece moulded plastic cells are best.
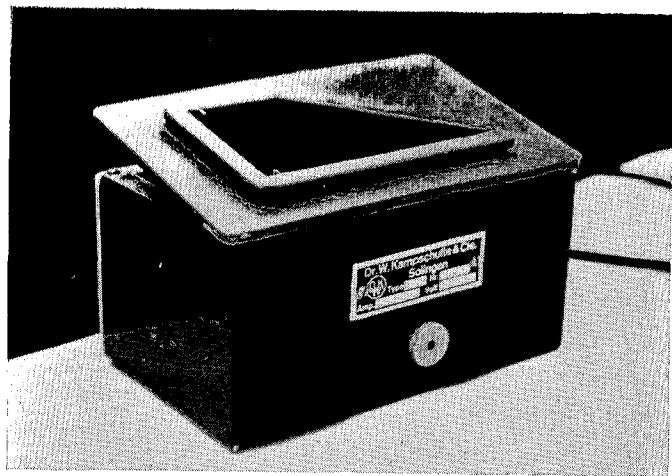
Fig. 8. 250 ml Hull cell of German manufacture with electrically heated water bath.
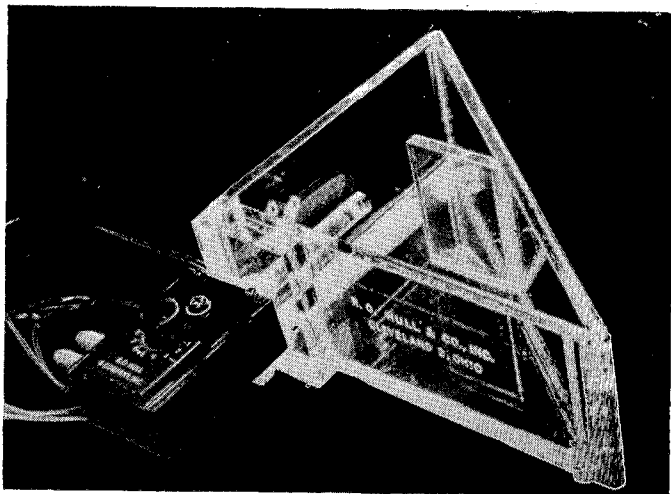
Fig. 9. 534 ml American Hull cell fitted with quartz immersion heater and thermostatic control.

Temperature and agitation

For temperature control either a water bath (see Fig. 8) or thermostatically controlled quartz immersion heaters (see Fig. 9) can be employed.

The R. O. Hull Co. also make a variable speed reciprocating agitator to closely simulate cathode rod agitation (Fig. 10).

Anode

As can be seen from the illustrations, the anode, which is $2\frac{1}{4}$ in $\times$ $2\frac{1}{2}$ in, is fitted closely to the cell wall. Normally it is flat and occupies the full cross section of the cell. Where the solution being tested is likely to give rise to high anode polarization, the anode will need to be constructed from gauze or from corrugated material to give an increased superficial area (see Fig. 11 ; see also Figs. 198 - 200). Its thickness must not exceed 0·2 in and its height should be such as to leave sufficient area over the solution level to take the electrical connections. The choice of anode material depends on the solution under test ; anodes are in fact made of brass, cadmium, copper, lead, nickel, tin and zinc and, for precious metal plating, in stainless steel, platinum and silver.

Fig. 10. Hull cell agitator to simulate cathode rod agitation in the Hull cell.

Fig. 11. Flat and corrugated Hull cell anodes complete with lead wire.

Fig. 12. Cathodes for the Hull cell.

The same anode should be used for all experiments on a given solution in order to eliminate the possible effect of differences in th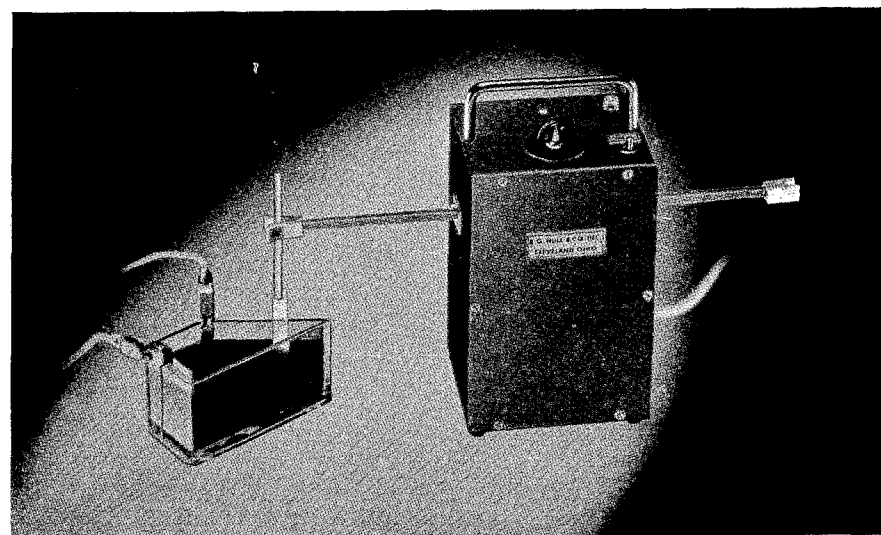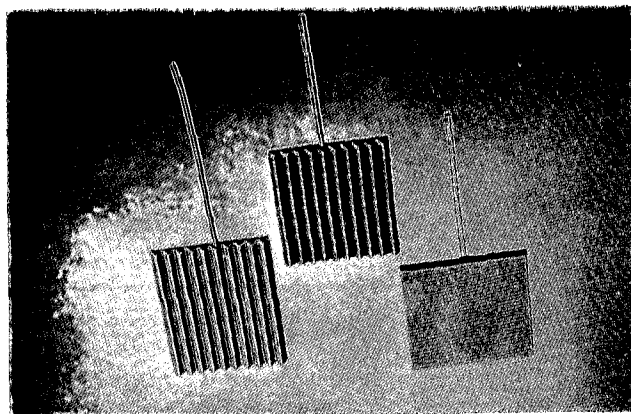e anode material. It has become common practice (in Germany) to surround the anode with filter paper, and if this is done at all it should be done for the entire series of experiments. However, it is generally preferable not to use filter paper but to clean and activate the anode in a suitable stripping solution for the metal.

When testing an electrolyte for the conditions of solution of the anode, the latter replaces the cathode panel in the cell. If a quantitative evaluation is required, the anode panel must be made to the full size of the standard cathode for the particular cell in use.

Cathode

The condition of the plating solution is judged from the appearance of the cathode after the test. Accordingly, the cathode material and its surface condition should ideally be the same as that of the work which is plated in practice. Generally however polished brass or steel is quite suitable, particularly if the brightness of the deposit is the only point of interest.*

It is well known that the surface composition and condition of the basis metal can have a most considerable effect on the plating obtained. It is important therefore that these factors be standardised. The R. O. Hull Co. supply standard cathodes in zinc plated semi-bright steel (No. 3 finish) which is ideal for cadmium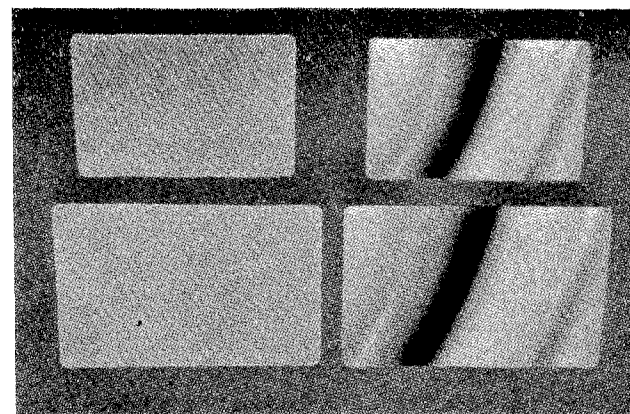 and zinc or in highly polished brass, protected by peel-off lacquer, which is suitable for testing bright brass, bright copper and bright nickel. The zinc coating is put on at the mill to prevent rusting of the panels before use and it is removed by dipping in 50% (vol) hydrochloric acid followed by rinsing, wiping of the panel with a clean cloth or wet paper towel and final rinsing just before use. In the case of polished brass panels, the protective plastic coating is first removed by grasping the corner edge with a knife or fingernail, then soaking the panel for approximately 20 seconds in a hot non-tarnishing brass cleaner or rubbing with a cotton wad or sponge soaked in trisodium phosphate or alkali cleaner, followed by rinsing in cold running water. When cleaning test panels, care must be taken to handle the panels by the edges only so as to prevent finger print smudges. If necessary, rubber gloves may be worn.

It is inadvisable to use a cathode more than once since stripping will in all probability materially alter the surface characteristics of the test piece.

Brass test panels are usually polished on the front surface only but in some circumstances it may be necessary to polish the back as well, as for example

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* R. O. Hull & Co. Inc. are not in entire agreement with this and always prefer to carry out a test on a substrate, be it basis metal or electrodeposit, as close as possible to that used in practice. Steel is recommended for testing cadmium and zinc. For nickel either a steel panel or a bright polished brass panel is used. When testing chromium solutions the panel is first plated with bright nickel and then rinsed and used in the Hull cell test. If it is a question whether the chromium or the bright nickel is the source of the problem, the panel is first nickel plated in the Hull cell using the bright nickel plating solution in question, and then tested in the chromium plating solution in another Hull cell.

when it is required to observe the tendency to etching on very low current density areas.

Hull cell test panels are made in two sizes, one to fit the 250, 267, 320 and 534 cells and the other for the 1000 ml cell and the Hanging Hull cell. It fits closely to the cell wall and its height should be such as to stand out of the solution sufficiently to make the electrical connections. Its thickness should preferably be 0·5 ± 0·1 mm but it can be up to 1 mm.

Current supply, control and measurement

For operation of the Hull cell a source of direct current is required capable of supplying 3 amps (or 5 amps in the case of 1000 ml cell); the maximum voltage ever likely to be required is 18 volts though normally it will be very much less than this.

To supply this direct current use can be made of either car batteries or small transformer/rectifier units. Since current ripple can affect the structure of an electrodeposit, it is important if a rectifier is used that the amount of ripple does not exceed 15%; an ordinary battery charger is therefore unsuitable. Three-phase rectifier units incorporating valve smoothing circuits have been widely employed in the past. However, even these are affected by mains voltage fluctuations such as may occur in any works laboratory and the modern tendency therefore is to use transistorised mains units which supply a constant voltage direct current, independent of either loading or mains voltage and which is practically free from ripple. An arrangement for constant voltage or constant current density control is sometimes used as an additional refinement.

When a lead accumulator is used to supply the power for the Hull cell it is recommended to arrange two 6 volt car batteries as shown in Fig. 13. This arrangement will usually provide sufficient current for the 250, 267 or 320 ml Hull cell but is less convenient than a transformer/rectifier unit.

Whichever method is employed means must be provided for controlling and measuring the current passed by the cell. The regulator should operate over 100% of the range and be stepless. Variable resistances can be used though in the case of a rectifier unit 100% stepless control through an auto-transformer is to be preferred.

Resistances should be selected in such a way that

$$R = \frac{\Delta V}{I_{min}} \ [\Omega] \qquad\qquad (1)$$
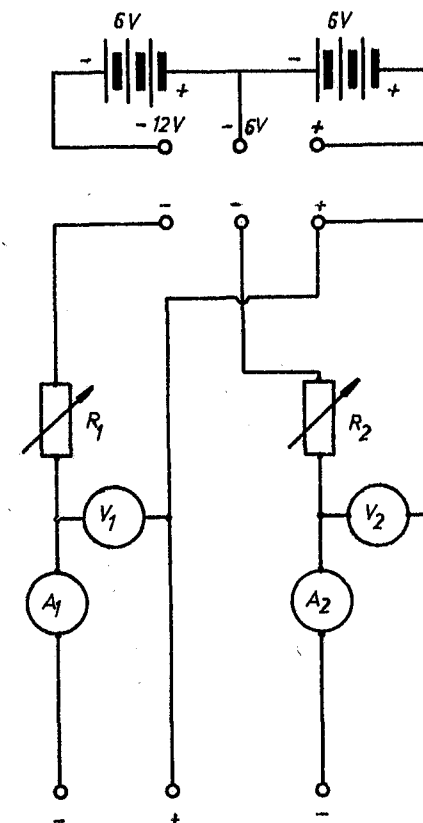
Fig. 13. Example of a circuit for Hull cell current supply using lead accumulators.

R₁   Variable rheostat with 'off' position, 6 ohms, 6 amperes
R₂   Variable rheostat with 'off' position, 30 ohms, 5 amperes
A₁   Ammeter, 10 amps, divided into 0·2 amp units
A₂   Ammeter, 6 amps, divided into 0·2 amp units
V₁   Voltmeter, 15 volts, divided into 0·2 volt units
V₂   Voltmeter, 6 volts divided into 0·2 volt units.

where

ΔV = the largest required voltage drop in volts and
I_{min} = the lowest required current in amperes.
The maximum current which can pass is taken as the loading.

Fig. 14. *Circuit diagram of resistance control in the Hull cell apparatus shown in Fig. 1.*
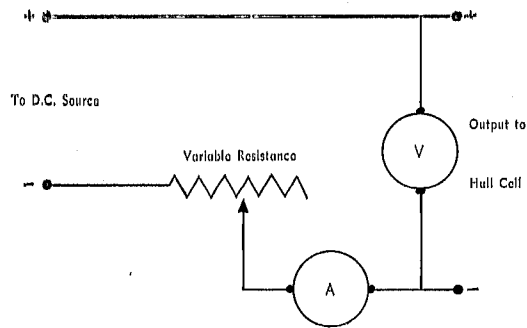
All the experiments described up to p. 90 were carried out using car batteries connected as shown in Fig. 13. The experiments on quality testing of nickel salts were conducted with the aid of a mains unit while Dr. Heyes (see p. 109) conducted his investigations with an electroplating rectifier with a ripple smoothing arrangement.

Hanging Hull cell

A newer development, currently not available outside the United States, is the Hanging Hull cell (Fig. 15).

As its name suggests, this is a version of the Hull cell designed to be hung directly on the carrier bar or cathode rod of the plating tank and which will produce on the test panel a deposit showing the characteristics of the plating bath over the entire operating current density range, thus combining most of the features of the standard Hull cell with the advantage of testing under production conditions. It consists of a 0 to 50 amp Perspex-encased ammeter hermetically sealed to a Perspex-encased 24 in or 32 in copper stem which, at the top, forms the cathode bar hook and at the bottom holds a Perspex Hull cell which in this case comprises a V-shaped box holding the larger size cathode as used in the 1000 ml Hull cell.

It is operated in much the same way as the standard Hull cell and the results are comparable for comparable current densities. It should however be remembered that the Hanging Hull cell panel may be plated at considerably higher currents than the standard Hull cell panel, thereby widening the current density range on the panel. For testing barrel solutions, the empty stationary barrel is submerged, the loading panel removed, and the Hanging Hull cell

held in the barrel, electrical contact being made with a flexible lead to the cathode rod.

Since the Hanging Hull cell operates directly in the plating solution, a much closer picture of the actual plating range present in the bath is obtained on the test panels than in the laboratory Hull cells. This is especially true in chromium plating solutions where the current densities found in production may not be duplicated in the 267 and 1000 ml Hull cells.

Among the most important uses of the Hanging Hull cell is the determination of the source of trouble in a sequence of plating operations. By comparing the panels obtained by cleaning and pickling the test panels in the plating set-up with those obtained using freshly stripped steel or freshly cleaned brass panels, any difficulty due to poor cleaning or pickling can be detected and traced directly to its source.
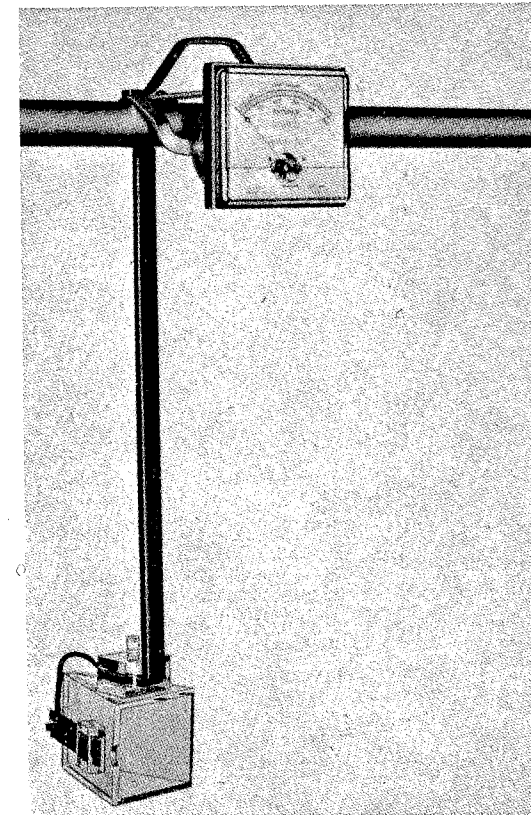

Fig. 15. *The Hanging Hull cell.*

By a similar set-up, the Hanging Hull cell may be used to test the effectiveness of post-plate bright or proprietary dips by comparing the panels obtained with those made in fresh dip solutions in a small container.

Another important use of the Hanging Hull cell is to make a current survey of a plating tank. A stripped panel is inserted into the cell head and the unit hung on various positions of the cathode rod. With the total voltage at a fixed value, the meter readings on the cell should be the same throughout the length of the cathode bar. If any variations in current reading are noticed, the cause may be poor anode contact or improper bussing of the cathode rod.

Modified Hull cell

The Modified Hull cell was developed for particular application to high current density solutions such as chromium plating solutions.* It consists of the standard (250, 267 or 320 ml) Hull cell in which $\frac{1}{2}$ in diameter holes have been introduced into the two parallel sides as shown in Fig. 16. On the long side of the cell the holes are kept towards the anode end, thus retaining the restrictive effect of the low current density areas. Exact spacing and size of the holes do not seem to be at all critical.
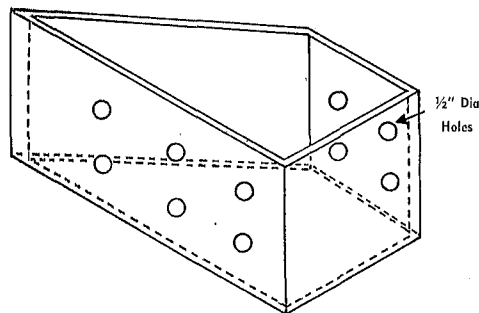

½" Dia Holes

Fig. 16. Modified Hull cell.

The Modified cell is used inside another vessel, such as a 7 in diameter crystallising dish filled to the cell solution mark with the solution under test or it can be placed directly in the plating tank. Operation of the cell at currents of 10 to 15 amps and temperatures of 115°F are possible with little temperature fluctuation as natural solution movement by convection currents produces a constant interchange of solution through the holes. Slow stirring helps and, unless of a very violent nature, does not appear to have any effect on the deposit.

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* J. Branciaroli. *Plating,* 1959, 46, No. 3, 253 - 60.

CHAPTER 2

THE HULL CELL TEST
AND ITS INTERPRETATION

Current distribution on the test panel

TO BE effective the current distribution on the test panel should cover a wider range of current density than that which is encountered in practice with the solution under test.

The primary current distribution on the Hull cell cathode follows a logarithmic curve and can be represented as

$$\text{C.D. at any point} = I \,(C_1 - C_2 \log L)$$

where L = distance along the cathode, I = total cell current and C_1 and C_2 represent constants which depend on the nature of the electrolyte. Hull determined these constants for a number of electrolytes, finding in general that they altered little from one electrolyte to another. In consequence, the values were averaged and general purpose formulae applicable to all electrolytes have been arrived at as follows:

for the 1000 ml cell

$$\text{C.D. at any point} = I \,(18\cdot8 - 28\cdot3 \log L)$$

for the 267 ml (and 534 ml) cell

$$\text{C.D. at any point} = I \,(27\cdot7 - 48\cdot7 \log L)$$

$$\text{(between the limits } L = 0\cdot25 \text{ and } L = 3\cdot25 \text{ in)}$$

where the current density is in amp/sq ft, I is in amperes and L is in inches.
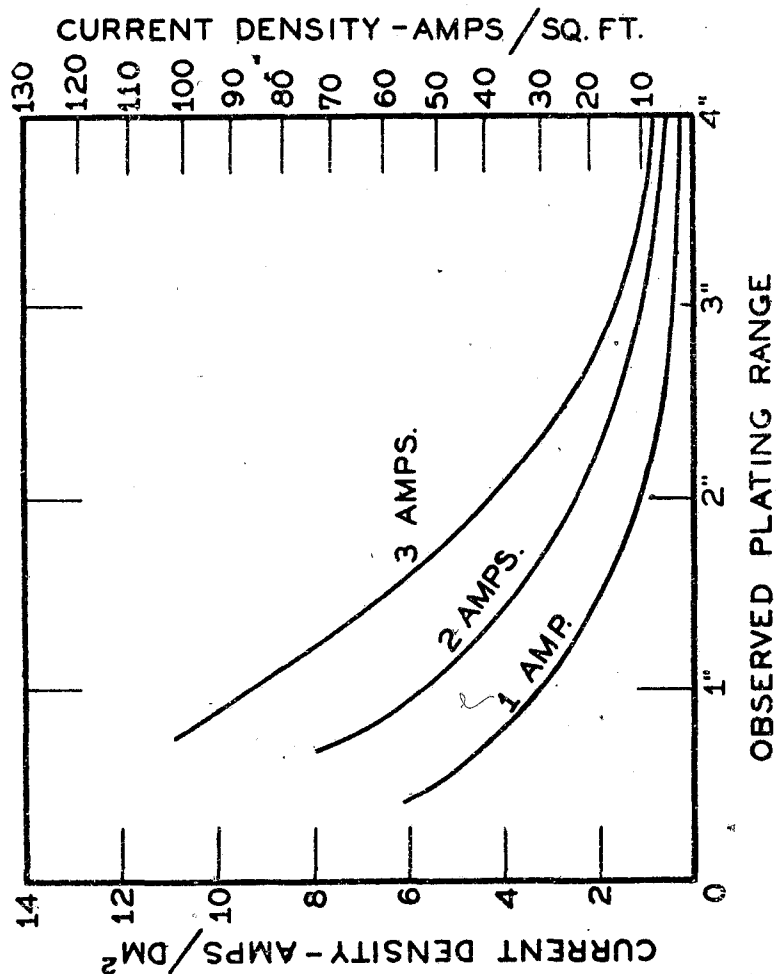
CURRENT DENSITY - AMPS / SQ. FT.

Fig. 17. Plating range of 267 ml Hull cell.

[H. J. Sedusky and J. B. Mohler

Since the 250 and 320 ml Hull cells differ from the 267 only in the depth of the solution employed, the formulae for these cells become: for the 250 ml cell

$$\text{C.D. at any point} = \frac{267}{250} \text{ I } (27 \cdot 7 - 48 \cdot 7 \text{ log L})$$

and for the 320 ml cell

$$\text{C.D. at any point} = \frac{267}{320} \text{ I } (27 \cdot 7 - 48 \cdot 7 \text{ log L})$$

Deviations from these are to be expected, particularly for cyanide electrolytes. If for instance the above equations lead one to expect a current density of say 30 amp/sq ft, this current density will generally not apply over the whole period of the test. When the current is first turned on the current density at this point will be 30 amp/sq ft but later cathode polarization will cause a change in the current density, or alternatively it may cause periodic current fluctuations. However, it has been shown in practice that these equations do give sufficiently close approximations of the local current density for most purposes.

In any case it must be remembered that for nearly all purposes the Hull cell test is a qualitative one and the specification of current density is usually quite unnecessary except by such general terms as low, medium or high.

When it is desired to refer to the actual current densities, graphs such as that shown in Fig. 17 may be constructed to avoid the often lengthy calculations involved in applying the above equations. If for instance one is using a 3 amp cell current in a 267 ml Hull cell, the current density at a point on the test panel 1 inch from the high current density end can be read off as 85 amp/sq ft, and at 2 inches from the high current density end, it is approximately 39 amp/sq ft and so on. These values can in turn be plotted on scales such as that shown in Fig. 19, which are even more convenient to use.

Hull cells can be left or right handed so that the high current density area can be at either end of the test panel. Generally, however, the cells are as shown in Figs. 2 - 4, p. 4 and the high current density area is on the left of the panel.

Metal distribution is again different from the current distribution since it also depends on the throwing power of the solution. The one exception is the acid copper plating bath in which the metal distribution and primary current distribution are always closely similar and secondary polarization effects are very small.

267 ml. and 534 ml. Hull Cells

	PANEL EDGE														
1 AMP.		40	30	25	20	15	12	10	8	6	4	3	2	1	0.5
2 AMPS.		80	60	50	40	30	24	20	16	12	8	6	4	2	1
3 AMPS.		120	90	75	60	45	36	30	24	18	12	9	6	3	1.5
5 AMPS.		200	150	125	100	75	60	50	40	30	20	15	10	5	2.5

TOTAL CURRENT

1000 ml. Hull Cell

	PANEL EDGE												
1 AMPS		90	60	45	36	30	24	18	15	12	9	6	3	0.6
2 AMPS.		150	100	75	60	50	40	30	25	20	15	10	5	1

TOTAL CURRENT

Fig. 19. Current density scales for the 267 ml, 534 ml and 1000 ml Hull cells (actual size). Current density in amp/sq ft. (R. O. Hull & Co. Inc.)

Test procedure

The first essential in making a Hull cell test on a plating solution is to obtain a truly representative sample. The best way of doing this is to use a sampling tube which is simply a Perspex, polythene or PVC tube ¾ in inside diameter and perhaps 4 ft long brought to a coarse jet at the lower end. Still solutions must be mixed with a plunger to avoid layering. It is important to measure the solution depth at the time of sampling in order that the volume in the vat can be estimated accurately before calculating the amounts of any additions that have to be made.

If chemical analysis is to be carried out (and Hull cell plating tests are not to be regarded as eliminating the necessity for occasional chemical analysis) such analysis should be made at this stage and the composition of the bath corrected accordingly before commencing the Hull cell test.

Different operators prefer slightly different ways of making a Hull cell test (the method given here differs slightly from that described in DIN 50 957). First the cell is cleaned; if more than one kind of plating bath is tested regularly, one cell should be used exclusively for each type of bath to avoid contamination of one bath sample by another. Next the temperature of the cell, and that of the water jacket if used, is adjusted to the test temperature. At the same time the electrolyte is warmed in a beaker to the same temperature and transferred to the cell to reach just below the solution level mark.

The anode should now be cleaned and the cathode prepared as already described. Both electrodes are then placed in position in the cell, connected electrically and a small current applied immediately; in some cases it will be better to connect and switch on the current before placing the cathode in the electrolyte. The arrangement of electrodes in the various Hull cells is shown in Fig. 20.

250,267 and 320 ml Hull cell
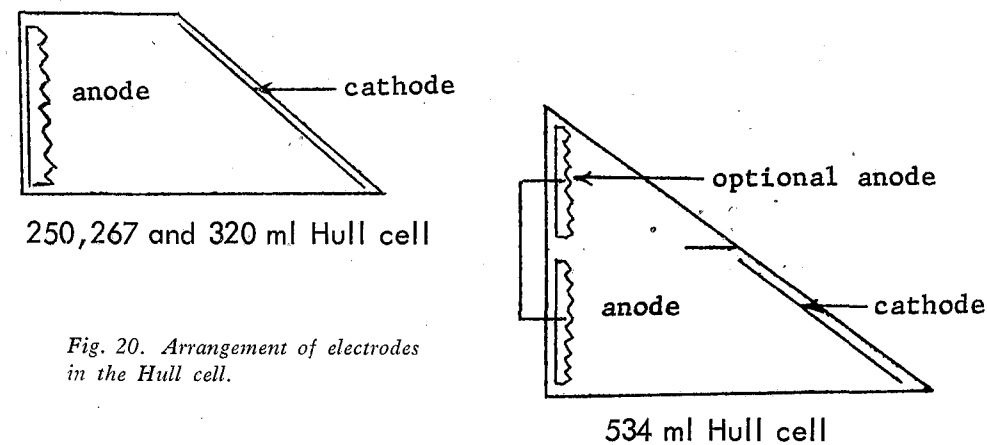
534 ml Hull cell

1000 ml Hull cell

Fig. 20. Arrangement of electrodes in the Hull cell.

Electrolyte is then added to bring the level in the cell exactly up to the mark (an error of ± 10 ml will invalidate the equations and diagrams for current distribution given above) and the temperature adjusted to ± 1°C. The current is then regulated to the selected amperage and electrolysis allowed to proceed for the predetermined time. The best time depends on the electrolyte and of course on the current density employed and is best determined in the light of one's own experience. DIN 50 957 recommend 4 minutes ± 10 seconds for bright chromium plating and 15 minutes ± 0·5 minutes for all other plating solutions. In Britain and America, however, 5 minutes is more usual for nickel, zinc and cadmium, 5 to 10 minutes for copper, brass, tin and silver and 4 minutes for chromium. Very short times or low current densities may be used for special purposes, for example, to investigate covering power. Whatever time is decided upon it must be adhered to rigidly if results are to be duplicated ; a timer is a useful accessory.

Experience has shown that attempts to stir the solution during the test are not to be recommended. If agitation of the electrolyte is considered essential this can be achieved by moving a glass rod thermometer to and fro in front of the anode at a rate of, say, one oscillation per second or, better still, by using the Hull cell agitator already described (Fig. 10). DIN 50 957 recommends that a motor-driven stirrer should be employed close to the cathode surface. The Author has found however that movement of the solution near the anode is less undesirable. This is due to the fact that the anode polarization is usually much higher than that of the cathode and hence it is easier to maintain a constant current density by the recommended method.

In all cases it is recommended to prepare a new solution sample for each Hull cell test, as the composition of the solution is altered by even a short period of electrolysis.* This can be readily appreciated when it is considered that a test with 250 ml of solution in which 3 amps are applied for 15 minutes corresponds to a current loading of 3 amp-hours per litre, which in many cases is equivalent to the loading of a production plating bath for a whole day. For the same reason the time of electrolysis should also be chosen to be as short as possible as this will minimise changes in composition during the experiment.

After the test has been completed the current is switched off, the cathode panel is removed immediately from the cell, rinsed thoroughly and dried. A suitable method of drying the panel is which avoids staining is to dip it in alcohol followed by air drying.

The test panel is inscribed with the type of electrolyte, the date of the test and the operating condition and is given a number. Small stick-on labels are suitable for this purpose.

Interpretation of test results

A test on a cold nickel bath using a brightener might produce a plate such as that shown in Fig. 21. The high current density end of the plate is at the left. The area A is dark and rough, B is dull, C is bright and at D there is little or no deposit. The lines from the top to the bottom of the plate marking the zones between A and B and between B and C curve towards the low current density end. This is due to interruption of the flow of solution along the cathode by the bottom of the cell, but it does not interfere with the interpretation of the results.
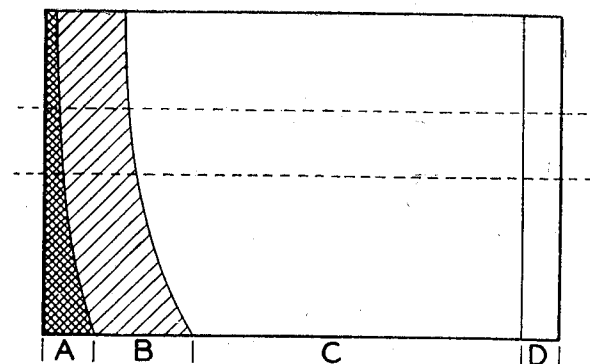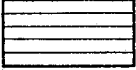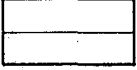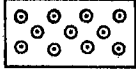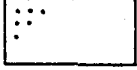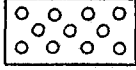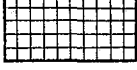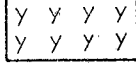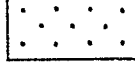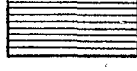

Fig. 21. Typical Hull cell test plate of a cold nickel bath with brightener (H. J. Sedusky and J. B. Mohler).

A good scheme for filing typical results for reference purposes is to sketch the appearance of only that part of the plate observed between the dotted lines. A note book entry would then appear as in Fig. 22. For convenience in making note book entries, codes have been devised for indicating the appearance of the different areas on the test plates, and these are shown in Fig. 23.

Fig. 22. Note book entry of a Hull test plate (Sedusky and Mohler).

* The R. O. Hull Co., while agreeing with this statement, say that up to three tests, sometimes more, are possible on one sample in the small Hull cell and up to 5 in the 534 ml Hull cell.

bright

semi-bright

dull

streaky, patchy

pitted

blistered

rough, burnt

powdery

brittle, cracked

uncoated

Commonly accepted code   According to DIN50957

Fig. 23. Codes for indicating the appearance of the different areas on test plates.

If the purpose of the test is to evaluate the effect of addition agent concentration in a new bath, the total current used should be that which will give the widest possible bright range. For instance, the plates shown in Fig. 25 might be obtained for total currents of 1, 2 and 3 amperes. It is seen that as the total current is increased, the apparent bright range (physical spread) shifts towards the low current density end of the plate. It is also seen that in this particular case a total current of 2 amperes gives the widest bright range with respect to the proportion of test panel covered.
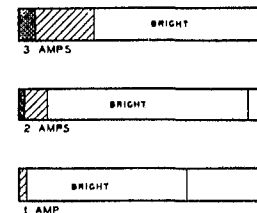

Fig. 25. Effect of total current on plating range. In this particular case the widest bright plating range is obtained at a current of 2 amperes (Sedusky and Mohler).

Interpretation of the test panel is then carried out with the aid of a diagram or scale to correlate current density (see Fig. 19, p. 20) and by comparison with previously-prepared test panels and/or note book entries in the light of experience. Unless the investigator has sufficient experience to permit him to interpret the result of a single test, he will obtain more reliable information by first carrying out control tests in which he changes one of the parameters of the plating conditions.

Hull cell tests are however by no means confined to judging the appearance of the deposit. Such properties as hardness, ductility and metal distribution can also be investigated and the effect of current density variations on such properties can then be ascertained.

CHAPTER 3

CHROMIUM PLATING SOLUTIONS

THE ANALYTICAL determination of the sulphuric acid concentration of a chromium plating solution is one of the most difficult and lengthy analytical procedures used in the plating laboratory. While the Hull cell method does not give the sulphuric acid content in terms of grams per litre, it does indicate the $CrO_3 : H_2SO_4$ ratio. Thus if the CrO_3 concentration is maintained by observation of the solution density, then it is possible to control a chromium plating solution by means of a hydrometer and a Hull cell.

Test procedure

The test procedure recommended by the R. O. Hull & Co. Inc. is to strip the zinc from a zinc plated steel test panel and prepare in the usual way, bright nickel plate for 2 minutes at $2\frac{1}{2}$ amps (do not leave the steel plates in water for a long period of time before nickel plating), rinse, and plate in chromium plating solution in the Hull cell for 4 minutes at 5 amps. If the $CrO_3 : H_2SO_4$ ratio is optimum and the bath is normal with respect to trivalent chromium, the plate will be covered with chromium to within $\frac{1}{2}$ to $\frac{3}{4}$ in from the low current density end of the plate and will show little or no iridescence on the unplated area. If the deposit is spotty, the sulphate is very low; if rainbows of brown oxide are present on the uncovered nickel, the sulphate is somewhat low. The test may then be repeated after increasing the sulphate content. If the plating range is narrow but no iridescence is noted, the sulphate content is too high for the chromic acid concentration.

Corfe* prefers to use two panels, one of polished brass at 5 amps for 3 minutes and one of polished or bright nickel at 10 amps for 1 minute. The brass panel will clearly indicate the presence of chloride contamination for while a panel from a solution free from chloride will not show signs of etching, a trace of this impurity (0·01 gm/litre) will etch the back of the panel. As the chloride increases, the etching spreads to the front of the panel and, at the same time, the covering power of the chromium solution decreases. Small additions of silver oxide to the cell will precipitate the chloride and eventually an etch-free panel will be obtained.

Corfe then tests the nickel plated panel. At this stage, as the chromium solution is in question, it cannot be left to chance that the bright nickel panel may be passive. It is, therefore, advisable to lightly polish the panel, which should then show a chromium coverage between 80 and 90 mm across the panel. Generally it is difficult to determine metallic impurities precisely as the panel will show a lowering of covering power as the impurities increase in concentration. However, fairly heavy contamination with copper and zinc can often be traced if the panel is first plated in a Hull cell containing nickel plating solution at 5 amps for 5 minutes. The nickel deposit is very thin at the low current density end and is often removed by a chromium solution contaminated by zinc or copper. Dilution, or raising the concentration of the bath by the addition of pure major constituents, is the only cure.

It should be remembered that poor rinsing from a bright nickel solution will result in nickel, boric acid, sulphate and chloride entering the chromium bath; all these are troublesome impurities resulting in lowering of covering power.

A low catalyst ratio may give a panel showing good coverage but iridescence will be present at the back, and possibly on the front, at the low current density end. In the case of self-regulating baths, a white patchiness appears but no iridescence. Small additions of pure sulphuric acid to the conventional, or catalyst salt to the self regulating, solution in the cell will indicate the amounts which can be added safely. A high catalyst ratio will result in a panel showing poor coverage.

Corfe points out that a reasonable panel will not guarantee good results from a barrel chromium solution which is of necessity operated under extremely adverse conditions.

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* C. F. Corfe in ' Control in Electroplating ', Robert Draper Ltd., Teddington.

Test results

The sequence of photographs produced in this chapter was obtained by tests on a production chromium plating bath. In the low current density areas of the work plated in this solution, various colour shades were visible.

The test conditions were as follows:

Cathode: brass sheet, $100 \times 70 \times 0.5$ mm, polished to mirror finish, degreased with Vienna lime, suspended without current.

Anode: lead sheet, cleaned by brushing before each experiment, suspended against a scrap sheet while the current was on.

Electrolyte: Sample from production plating bath showing the following analysis:

CrO_3	410 g/l
H_2SO_4	0.9% (relative to the CrO_3 concentration)
Cr_2O_3	6 g/l
Fe	5 g/l
Ni and Cu	traces

Cell current: The cell current was 4.8 amp. Voltage varied with plating conditions.

Temperature: The initial temperature was 40°C in each experiment.

Plating time: 5 minutes per test.

The first panel was prepared by electrolysing the chromium plating solution as taken from the bath, and this panel was used for comparison (see Fig. 26). For the subsequent panels the sulphuric acid concentration was increased in stages by additions of 0.2 per cent H_2SO_4 (equivalent to 0.82 g/l H_2SO_4) until the sulphuric acid concentration had been doubled (see Figs. 27 to 31). The photographs are in a mirror-image relation to the original Hull cell panels, i.e., the high current density area is seen on the right hand side of the panel. It can be clearly seen that the streaks in the low current density area disappear as the sulphuric acid content is increased, while the throwing power is reduced.

Fig. 32 shows a panel obtained after adding 30 g/l chromic acid to the solution. This shows that the coverage is increased although streaks remain at the low current density side of the panel. Accordingly 30 g/l chromic acid together with 0.15 per cent sulphuric acid were added to a new sample of the solution. The effect of these two addition is shown in Fig. 33. Following this experiment, the plating bath itself was corrected by making these additions, and it gave good results.
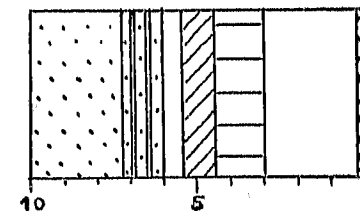
Fig. 26. Chromium plating bath (1)
Original bath sample
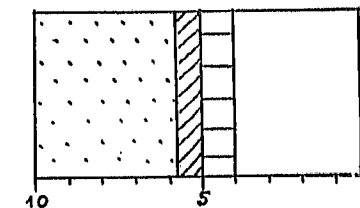4.8 amp   40 - 46°C   5.1 v   5 min
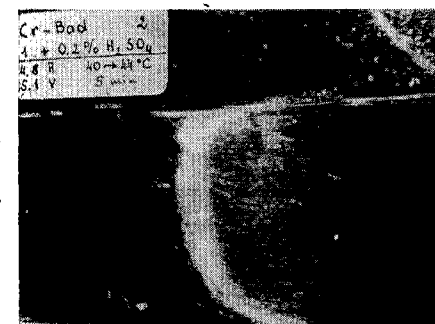

Fig. 27. Chromium plating bath (2)
Soln (1) + 0.2% sulphuric acid
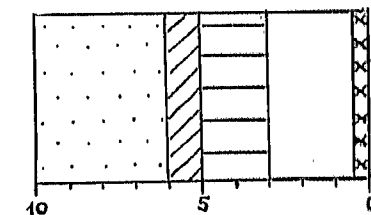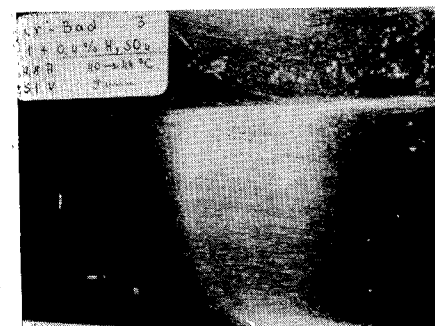4.8 amp   40 - 44°C   5.1 v   5 min

Fig. 28. Chromium plating bath (3)
Soln (1) + 0.4% sulphuric acid
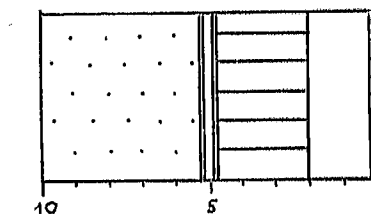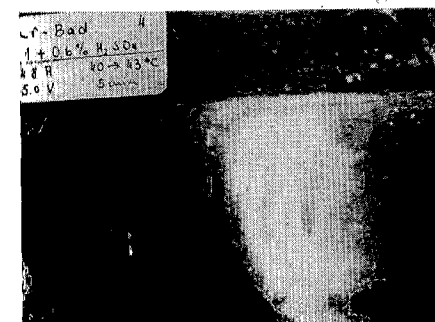4.8 amp   40 - 44°C   5.1 v   5 min

Fig. 29. Chromium plating bath (4)
Soln (1) + 0.6% sulphuric acid
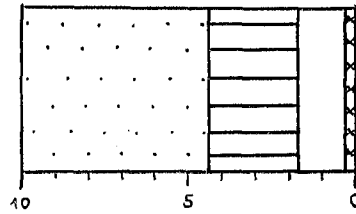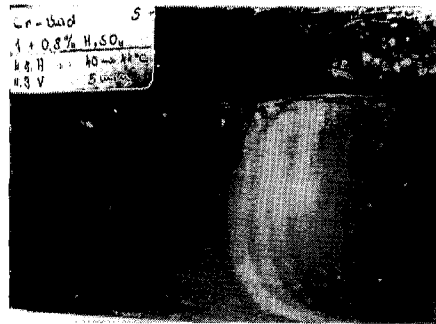4.8 amp   40 - 43°C   5.0 v   5 min

Fig. 30. Chromium plating bath (5)
Soln (1) + 0.8% sulphuric acid
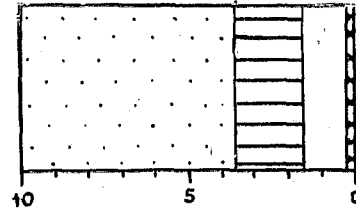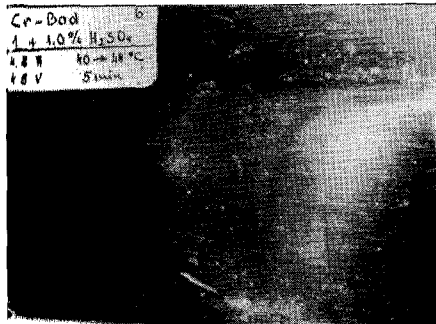4.8 amp   40 - 44°C   4.9 v   5 min

Fig. 31. Chromium plating bath (6)
Soln (1) + 1.0% sulphuric acid
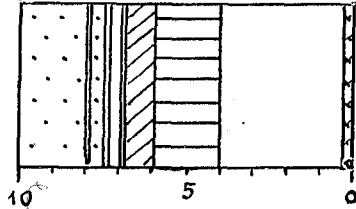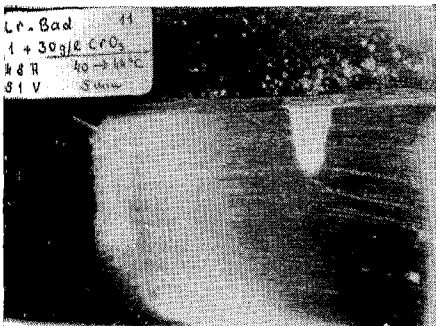4.8 amp   40 - 44°C   4.5 v   5 min

Fig. 32. Chromium plating bath (11)
Soln (1) + 30 g/l chromic acid
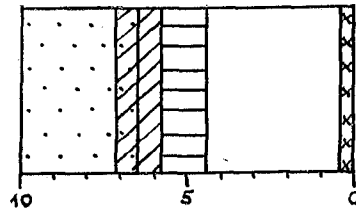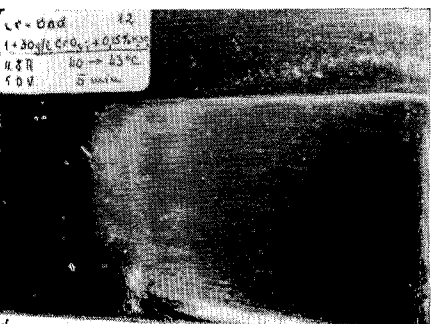4.8 amp   40 - 44°C   5.1 v   5 min

Fig. 33. Chromium plating bath (12)
Soln (1) + 30 g/l chromic acid +
0.15% sulphuric acid
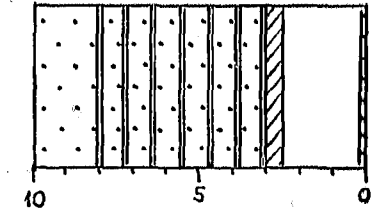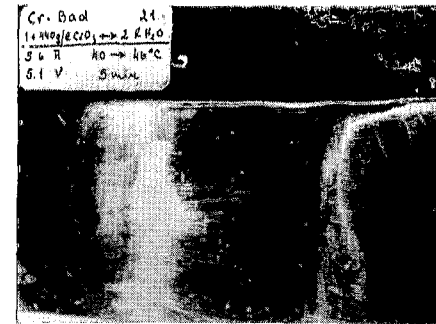4.8 amp   40 - 43°C   5.0 v   5 min

Fig. 34. Chromium plating bath (21a)
Soln (1) with sulphuric acid
concentration reduced to one half
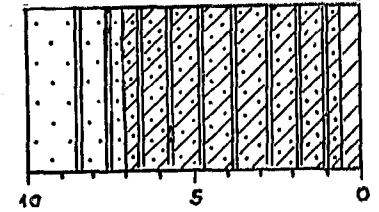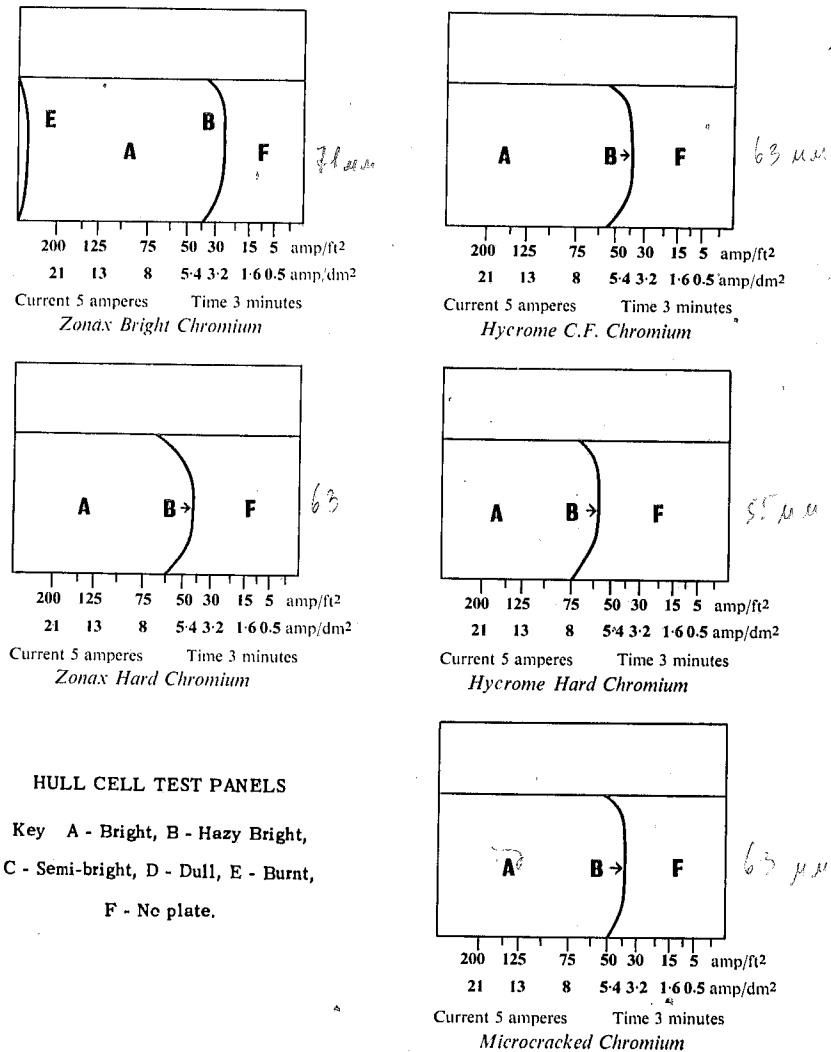5.6 amp   40 - 46°C   5.1 v   5 min

Fig. 35. Chromium plating bath (22)
Soln (1) with sulphuric acid
concentration reduced to one quarter
4.8 amp   40 - 45°C   5.0 v   5 min

Subsequently the sulphuric acid concentration of the solution was reduced to one half (see Fig. 34) and then to one quarter (see Fig. 35) of the nominal concentration. These panels clearly show that the covering power of the bath is reduced and the streaks in the deposit extend into higher current density regions of the panel. The panel shown in Fig. 35 shows that no coherent deposit is formed at all under these conditions.

It has previously been pointed out that while Hull cell test results will always show characteristic trends, they are specific to each individual plating solution. As an example of this Fig. 35a shows Hull cell test patterns for five proprietary chromium plating solutions of W. Canning & Co. Ltd. Zonax are standard solutions while Hycrome solutions are high speed formulations. It will be seen that there is no significant difference between the patterns for crack-free and micro-cracked chromium.

200 125   75   50 30 15 5 amp/ft2
21   13   8   5·4 3·2 1·6 0·5 amp/dm2

Current 5 amperes   Time 3 minutes
Zonax Bright Chromium

200 125   75   50 30 15 5 amp/ft2
21   13   8   5·4 3·2 1·6 0·5 amp/dm2

Current 5 amperes   Time 3 minutes
Hycrome C.F. Chromium

200 125   75   50 30 15 5 amp/ft2
21   13   8   5·4 3·2 1·6 0·5 amp/dm2

Current 5 amperes   Time 3 minutes
Zonax Hard Chromium

200 125   75   50 30 15 5 amp/ft2
21   13   8   5·4 3·2 1·6 0·5 amp/dm2

Current 5 amperes   Time 3 minutes
Hycrome Hard Chromium

HULL CELL TEST PANELS

Key   A - Bright, B - Hazy Bright,

C - Semi-bright, D - Dull, E - Burnt,

F - No plate.

200 125   75   50 30 15 5 amp/ft2
21   13   8   5·4 3·2 1·6 0·5 amp/dm2

Current 5 amperes   Time 3 minutes
Microcracked Chromium

Fig. 35a. Hull cell test pattern for five proprietary chromium plating solutions (W. Canning & Co. Ltd.). Zonax are standard solutions. Hycrome are high speed formulations.

CHAPTER 4

IMPURITIES IN BRIGHT NICKEL PLATING SOLUTIONS

IN ADDITION to impurities the Hull cell test will also indicate an abnormal boric acid content of a nickel plating solution, as demonstrated below. The Hull cell is not usually relied upon for nickel or chloride content nor for pH though low nickel will show as burned areas at high current densities, low chloride by gassing at the anode plus a low anode efficiency, high pH by a yellow tinge in the deposit which may be irregular and brittle at high current densities and low pH by gassing of the cathode combined with the production of a smoky blue or brittle deposit.

The bright nickel plating solution used in the following investigations had the following analysis:

Nickel (Ni^{++})	75 g/l
Chloride (Cl^-)	18 g/l
Boric acid (H_3BO_3)	40 g/l
pH	4·2

The solution was used with a proprietary brightener at 60 amp/sq ft, 5·5 volts and 55°C.

The operating conditions of the Hull cell were as follows:

Cathode: brass sheet (Ms 72) polished to a mirror finish, prepared by cathodic cleaning and acid dipping.

Anode: nickel anode, 5 mm thick, quality 'Schwerte S 51'.

Current: The total current used in the Hull cell test was such as to show the effect of the impurities clearly.

Temperature: 55°C.

Time of test: 10 minutes.

In testing the nickel plating solution described above, the panels (see Fig. 36) showed a fully-bright nickel coating within the current density range 130 to 20 amp/sq ft. At current densities below 20 amp/sq ft the deposit had a matt bloom. As the electrolyte did not contain any of the usual impurities, it was subjected to a complete analysis which showed contamination by 5 g/l manganese (Mn^{++}). The manganese content of the solution was due to earlier conversions of the bath. The removal of manganese from a nickel plating solution is a difficult and lengthy operation and, as the current density range within which satisfactory deposits were obtained was relatively wide, this action was postponed.

Copper contamination

In the experiments described below impurities were added purposely to a new electrolyte in order to learn how to recognise their influence on the appearance of the Hull cell panels.

Fig. 37 shows the effect of the addition of 1 g/l copper and Fig. 38 of 0·25 g/l copper added as $CuSO_4.5H_2O$. It is seen that copper contamination shows as a dark grey deposit in the low current density areas of the panel. This demonstrates that it is possible to remove copper from a nickel plating solution by plating out at low current densities. This is preferably carried out at a reduced pH and voltage, e.g. pH 2 and 0·9 volts, as under these conditions the deposition of nickel is inhibited. The cathodes should have as large a surface area as possible, and corrugated steel cathodes are frequently used for this reason. In this case the copper is deposited preferentially in the valleys of the corrugated sheet. The purification process can easily be supervised in the Hull cell by testing samples of the solution from time to time as purification proceeds.

Iron contamination

The next impurity to be added to the solution was 1 g/l iron (as $FeSO_4.7H_2O$). Fig. 39 shows the effect of this impurity at a total current of 1·8 amp and at pH 3·9. This panel shows that at current densities down to 5 amp/sq ft the presence of iron in the solution has little or no effect on the appearance of the nickel deposit plated under normal conditions. If, however, the total current through the Hull cell is reduced to 1 amp at the

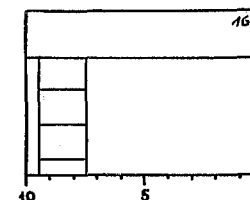Bright Nickel: and Copper Contamination

Fig. 36. Bright nickel bath (1)
Original condition
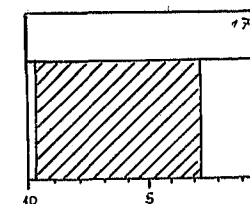2.0 amp   55°C   pH 4.0   5.6 v   10 min

Fig. 37. Bright nickel bath (11)
Soln (1) + 1 g/l copper
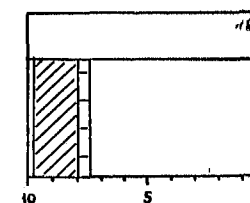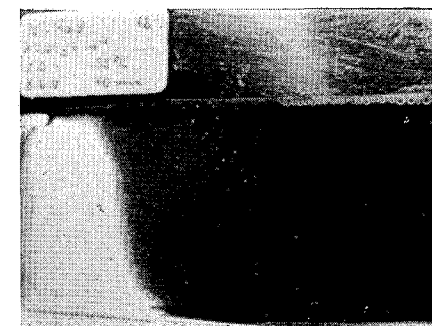2.0 amp   55°C   pH 4.0   5.6 v   10 min

Fig. 38. Bright nickel bath (12)
Soln (1) + 0.25 g/l copper
2.0 amp   55°C   pH 4.0   5.6 v   10 min

same pH (see Fig. 40) the matt current density range is shifted upwards. If the panel is placed on the diagram shown in Fig. 18 it is seen that the matt range still starts at 5 amp/sq ft.

The pH of a fresh sample was now reduced to 5·5 by adding nickel carbonate and panels were plated in the Hull cell at 2·0 amp (Fig. 41) and 1·0 amp (Fig. 42) respectively. It is clearly noticeable that the effect of iron contamination is much more marked at higher pH values. From this it is possible to conclude that if a nickel plating solution is contaminated with iron, the effects can often be counteracted without loss of brightness of the deposit by decreasing the pH and increasing the current density.

The accepted method of removing iron from a nickel plating bath consists of oxidising the ferrous iron to the ferric state by addition of hydrogen peroxide: *

$$2 \, FeSO_4 + H_2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2 \, H_2O \tag{3}$$
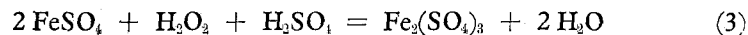
The trivalent iron is then precipitated by freshly precipitated nickel carbonate:

$$NiSO_4 + Na_2CO_3 = NiCO_3 + Na_2SO_4 \tag{4}$$

$$NiCO_3 + H_2SO_4 = NiSO_4 + H_2O + CO_2 \tag{5}$$
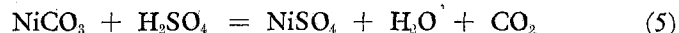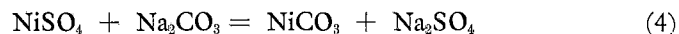
The equations show that both the reactions consume acid, i.e., that the pH value and thus the free hydroxyl ion concentration rises:

$$Fe_2(SO_4)_3 + 6 \, OH^- + 6 \, H^+ = 2 \, Fe(OH)_3 + 3 \, H_2SO_4 \tag{6}$$

(empirical hydrolysis equation)
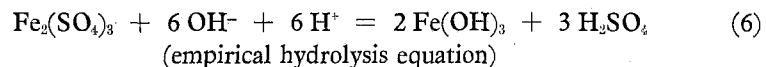
Colloidal brown ferric hydroxide is precipitated, and in order to ensure that it is not redissolved by the liberated free sulphuric acid and that the fine ferric hydroxide particles are truly precipitated, an excess of nickel carbonate is added. This raises the pH to approximately 6·3. After the plating solution has been filtered and brought back to the correct pH, the electrolyte is ready for use.

---

* Unless specifically indicated to the contrary by the supplier of the bright nickel solution being tested, hydrogen peroxide will usually deteriorate the brightener, thereby introducing further variable factors due to the absence of sufficient brightener to perform properly and/or by the presence of decomposition products. Generally speaking a high pH treatment with nickel carbonate, which of course will remove one half of the iron present, is usually adequate to determine whether iron is in fact causing the problem. If peroxide is used it would seem necessary to follow the peroxide - nickel carbonate treatment with a carbon treatment and replenishment of the brighteners.—Ed.
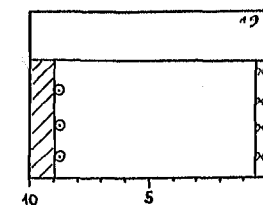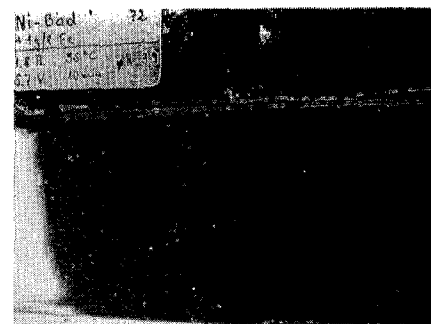
Iron Contamination

Fig. 39. Bright nickel bath (72)
Soln (1) + 1 g/l iron
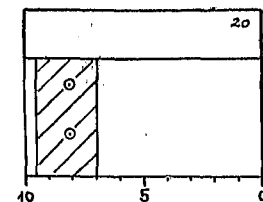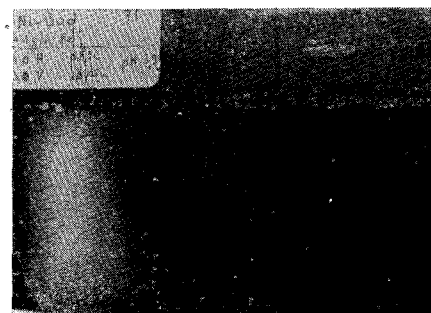1.8 amp   55°C   pH 3.9   5.7 v   10 min

Fig. 40. Bright nickel bath (71)
Soln (1) + 1 g/l iron
1.0 amp   55°C   pH 3.9   3.0 v   10 min
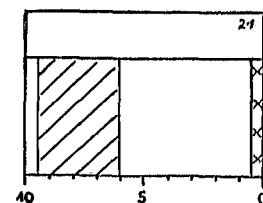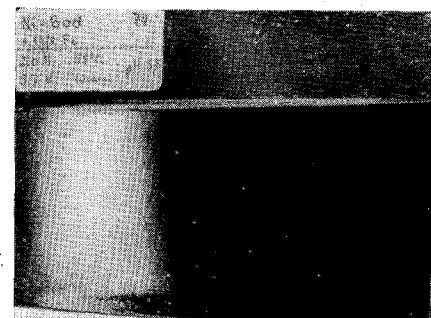

Fig. 41. Bright nickel bath (74)
Soln (1) + 1 g/l iron
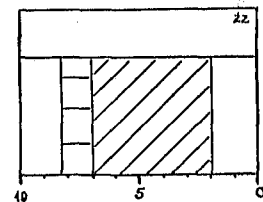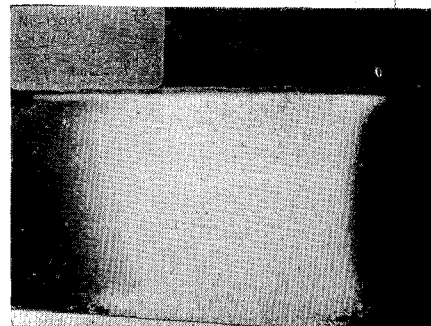2.0 amp   55°C   pH 5.5   5.7 v   10 min

Fig. 42. Bright nickel bath (73)
Soln (1) + 1 g/l iron
1.0 amp   55°C   pH 5.5   3.2 v   10 min

Fig. 43 shows a Hull cell panel obtained with the solution used for Fig. 42 after purification. This shows that most of the iron has been removed but that purification is not yet complete. If now the current density is increased and the pH value of the bath reduced, the effect of the impurity can no longer be observed (Fig. 44). At the same time it can be seen that the bloom caused by the presence of manganese has remained ; in other words, manganese is not removed by this method.

Effect of hydrogen peroxide

Hydrogen peroxide is sometimes added to nickel plating baths in order to oxidise certain compounds, such as iron, which are present as impurities. If the amount of hydrogen peroxide added is considerable, the solution becomes unsuitable for plating (see Fig. 45), producing nickel deposits which nickel deposits which tend to be brittle and cracked while at the low current density areas the coating may fail to cover altogether, i.e. the covering power of the bath is decreased drastically. As shown by Fig. 46, however, the hydrogen peroxide decomposes completely after the bath has stood for 20 hours.

Chromic acid contamination

Chromic acid is one of the most harmful impurities in nickel plating solutions and platers have good reason to fear the carry-over of chromium plating solution on plating racks. Chromic acid was added in progressively increasing concentrations to fresh samples of the nickel plating solution. The additions were made in steps of 10 mg/l starting at 0·01 g/l (see Fig. 47) up to 0·06 g/l (Fig. 52). 0·01 g/l corresponds to the addition of 25 ml of chromium plating solution to 1000 litres of nickel plating solution.

It is seen that chromic acid is harmful at all current densities. In the high current density areas, the nickel coatings are cracked, brittle and finally turn black. The high rate of hydrogen evolution results in the formation of nickel hydroxide. In the medium current density range a bloom is observed and cracked streaks appear in the coating, while in the low current density areas the coating tends to be brown in colour and under extreme conditions no deposit will be formed. At very high chromic acid concentrations, e.g. 1·75 g/l, no nickel is deposited. Figs. 45 and 51 are very similar. Both the additives are oxidising agents.
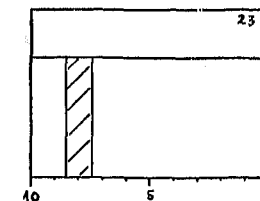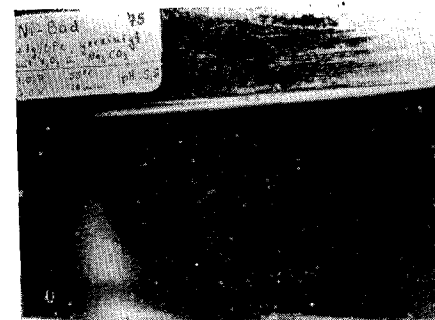
Purification Treatments

Fig. 43. Bright nickel bath (75)
Soln (1) + 1 g/l iron, purified with H_2O_2 and $NiCO_3$
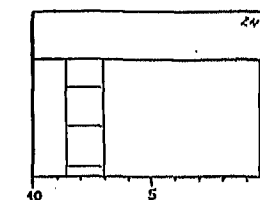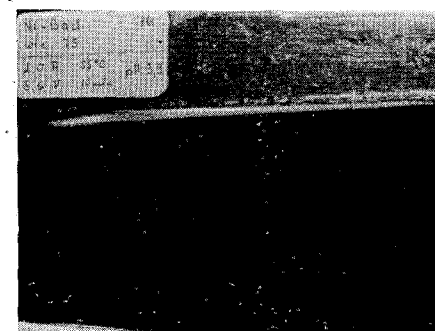1.0 amp 55°C pH 5.5 3.0 v 10 min

Fig. 44. Bright nickel bath (76)
Soln (75) as Fig. 43
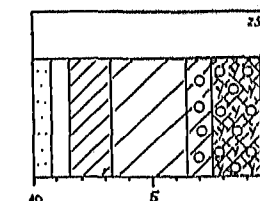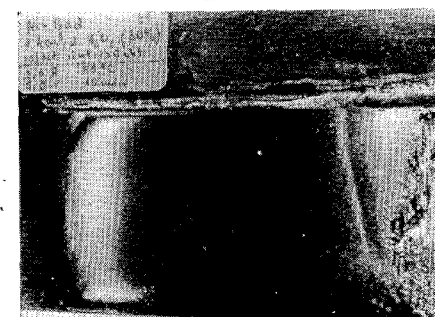2.0 amp 55°C pH 3.9 5.6 v 10 min

Fig. 45. Bright nickel bath (61)
Soln (1) + 4 ml/l H_2O_2 (30%),
tested without delay
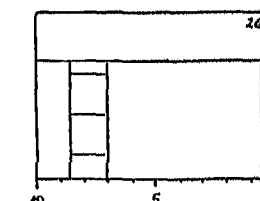2.0 amp 55°C pH 4.5 5.5 v 10 min
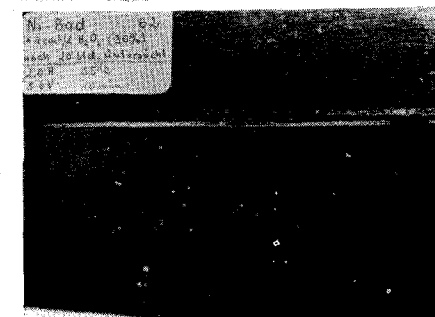
Fig. 46. Bright nickel bath (62)
Soln (61) tested after standing for 20 hours
2.0 amp 55°C pH 4.6 5.6 v 10 min

Chromic Acid Contamination
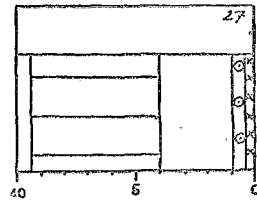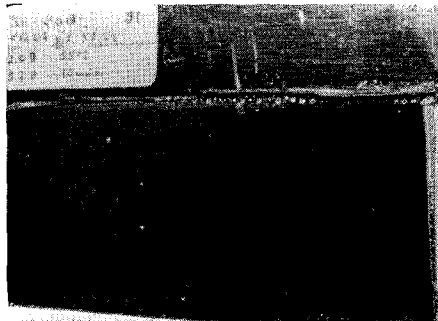
Fig. 47. Bright nickel bath (51)
Soln (1) + 0.01 g/l CrO₃
2.0 amp   55°C   5.7 v   10 min
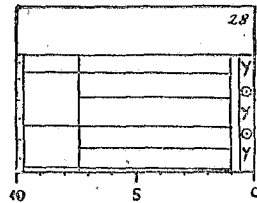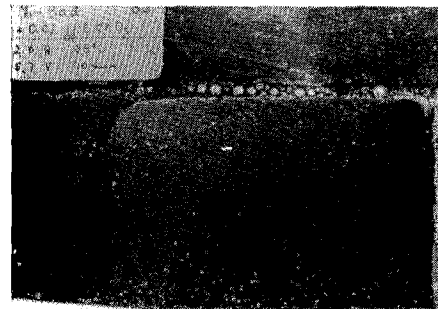
Fig. 48. Bright nickel bath (52)
Soln (1) + 0.02 g/l CrO₃
2.0 amp   55°C   5.7 v   10 min
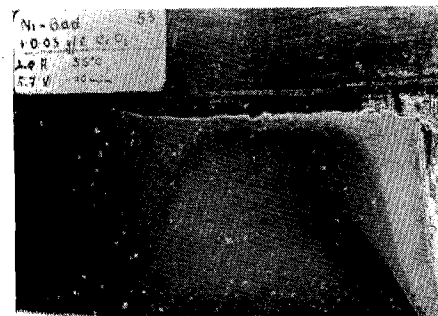
Fig. 49. Bright nickel bath (53)
Soln (1) + 0.03 g/l CrO₃
2.0 amp   55°C   5.7 v   10 min

continued

Fig. 50. Bright nickel bath (54)
Soln (1) + 0.04 g/l CrO₃
1.9 amp   55°C   5.7 v   10 min

Fig. 51. Bright nickel bath (55)
Soln (1) + 0.05 g/l CrO₃
1.9 amp   55°C   5.7 v   10 min

Fig. 52. Bright nickel bath (56)
Soln (1) + 0.06 g/l CrO₃
1.9 amp   55°C   5.6 v   10 min
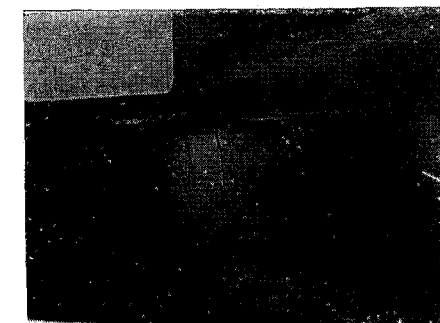
Fig. 53. Bright nickel bath (57)
Soln (1) + 1.75 g/l CrO₃
1.6 amp   55°C   5.6 v   10 min

Zinc contamination

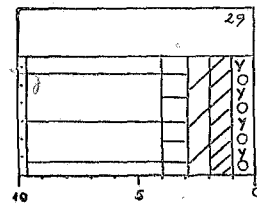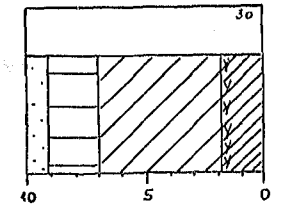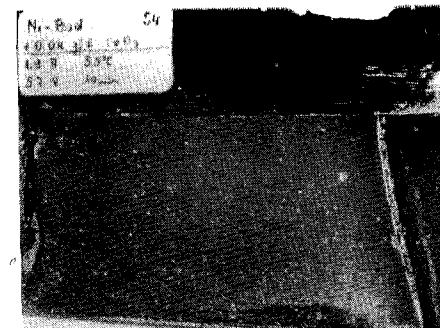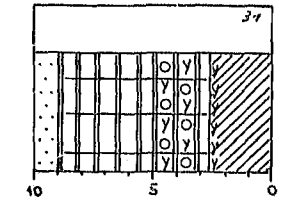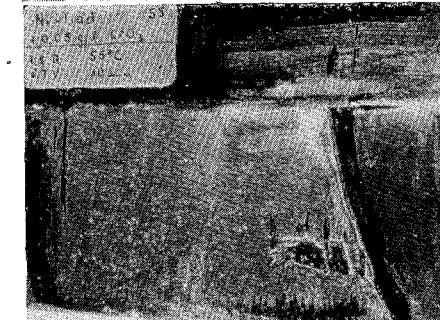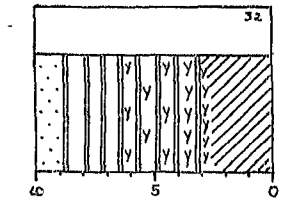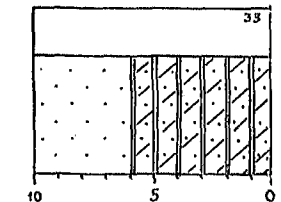Particularly in the nickel plating of zinc base die castings, the presence of zinc in the nickel plating solution may form an important source of contamination. The main effect of this impurity is seen as a black coloured deposit in low current density areas and as cracked and brittle coatings in the higher current density areas.

Fig. 54 shows the Hull cell panel of a bright nickel plating solution contaminated with 1 g/l zinc. On the basis of experience the panel was prepared using a low current density and a pH of 5·5. In the current density range corresponding to less than 6 amp/sq ft the coating was bright and streaked with black. Up to approximately 20 amp/sq ft it showed the well known 'zebra' stripes. At higher current densities a porous and cracked deposit was obtained. With experience it is possible to establish the correct conditions for black nickel plating from this experiment.

If the total current flowing through the Hull cell is increased to 2 amp at pH 5·5 neither the black coloration nor the 'zebra' stripes are very distinct (see Fig. 55). Up to 80 amp/sq ft the coating is cracked and matt, while at still higher current densities the deposit is bright, coarse in texture and brittle. If the pH is decreased to pH 3·9 and the Hull cell current is decreased to 1 amp, the range within which black deposits is plated lies above 30 amp/sq ft and the deposits are brittle and cracked. In the low current density range, the deposit has a bloom and shows areas which have not been covered. This would indicate that zinc can be removed from nickel plating solutions by plating out at 50 amp/sq ft at low pH values. The author has not tested this method but is of the opinion that, as in the more usual method of removing zinc with caustic soda, appreciable amounts of nickel would also be lost.

Cadmium contamination

Cadmium shows similar effects to those noted for zinc.

Zinc and Cadmium Contamination
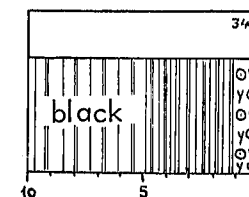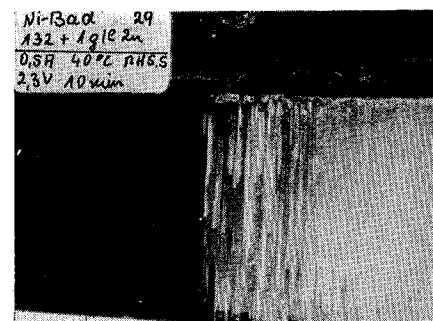
Fig. 54. Bright nickel plating bath (29)
(see Fig. 77)
Soln (132) + 1 g/l zinc
0.5 amp   40°C   pH 5.5   2.3 v   10 min
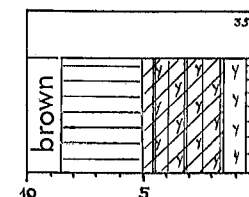
Fig. 55. Bright nickel plating bath (28)
Contaminated with large amount of zinc
2.0 amp   55°C   pH 5.5   5.7 v   10 min
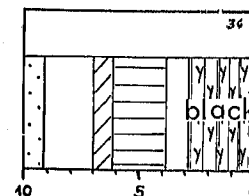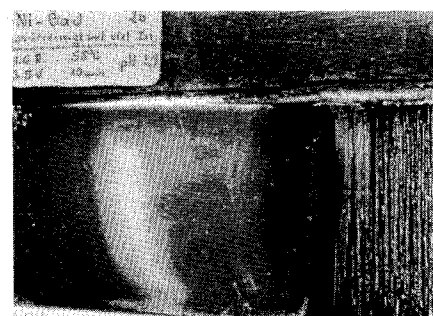
Fig. 56. Bright nickel plating bath (26)
Contaminated with large amount of zinc
1.0 amp   55°C   pH 3.9   3.5 v   10 min

Lead contamination

If a bright nickel plating bath is used in a lead lined tank there is the risk that lead will dissolve in the solution. The tank frequently acts as a bipolar electrode, nickel being deposited behind the anodes and lead being dissolved from the bottom of the tank below the work. Although both lead sulphate and lead chloride are only sparingly soluble, the slight amounts which go into solution are sufficient to cause visible deterioration of the nickel deposit.

At the low current density range red-brown to dark-brown stains appear (see Fig. 57). The risk is magnified if the amount of lead going into solution is increased by the formation of complex compounds. While at high pH values the appearance of Hull cell test panels plated under these conditions is similar to those obtained in the presence of chromic acid contamination, at pH 4 coloured areas appear in the low current density areas (see Figs. 58 to 61).

Lead Contamination
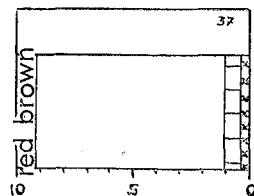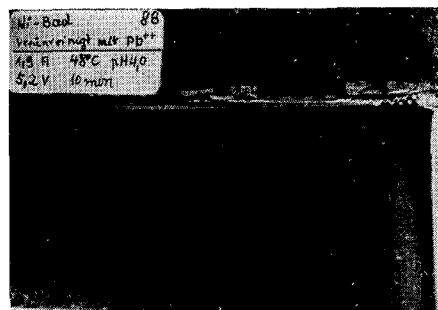
Fig. 57. Bright nickel bath (88)
Contaminated with lead
1.9 amp   48°C   pH 4.0   5.2 v   10 min

continued

Lead Contamination (continued)
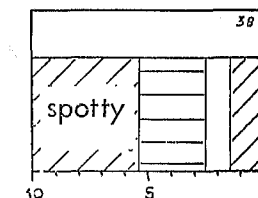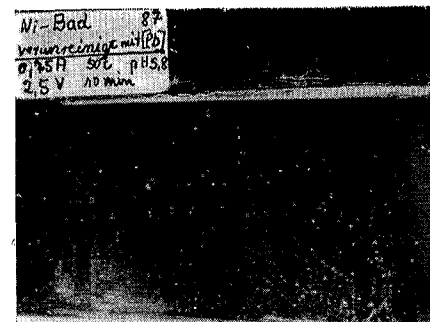
Fig. 58. Bright nickel bath (87)
Contaminated with lead, complexed
0.75 amp   50°C   pH 5.8   2.5 v   10 min
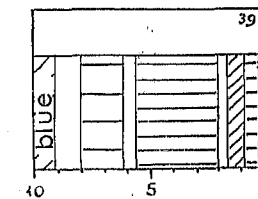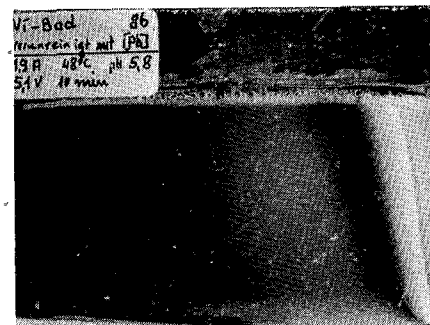
Fig. 59. Bright nickel plating bath (86)
Contaminated with lead, complexed
1.9 amp   48°C   pH 5.8   5.1 v   10 min
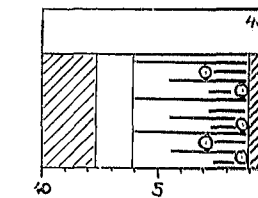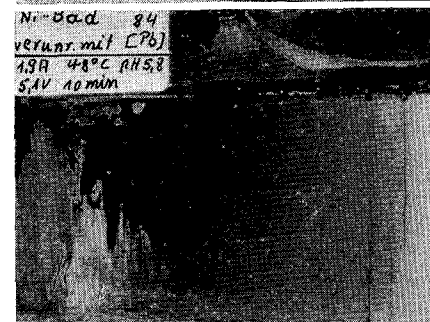
Fig. 60. Bright nickel plating bath (84)
Contaminated with lead, complexed
2.0 amp   52°C   pH 4.0   4.2 v   10 min
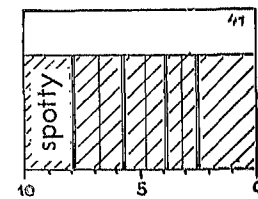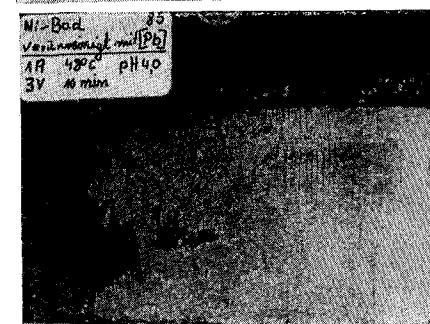
Fig. 61. Bright nickel plating bath (85)
Contaminated with lead, complexed
1.0 amp   48°C   pH 4.0   3.0 v   10 min

Other impurities and plating defects

A plating solution which is contaminated with solid impurities will usually deposit porous deposits. Fig. 62 shows the influence of dirt which has entered the plating tank. As shown in this photograph, this condition may also cause a reduction in the brightness of the nickel coating.

The effect of organic impurities is seen in Fig. 63. This panel was plated in a solution to which the wrong brightener had been added. The deposit was leaden in appearance and in the high current density areas the coating was brittle and cracked. In most such cases the reverse side of the panel showed dark brown stains (see Fig. 64) ; in the present case the anode was turned a deep black colour. It is impossible to cover in detail even a proportion of the different phenomena which can result from contamination with organic materials. If any specific organic impurity is suspected this can be checked by adding a little of the compound to a fresh sample of the plating solution and testing in the Hull cell under the same conditions. Care must be taken not to add too much of the impurity at first, as even small concentrations of the order of milligrams per litre may cause visible effects.

Fig. 65 shows the effect of low boric acid concentration. In the high current density range the deposit becomes so brittle that it breaks up. At the same time the pH rises markedly, in the present case from pH 4·0 to 4·5. Fig. 65 was purposely produced in a solution in which the concentration of the primary brightener was low, to ensure that the embrittling effect was not due to excess of this brightener (compare Fig. 72).

Other Impurities ; Low Boric Acid
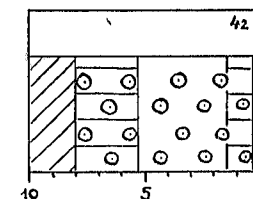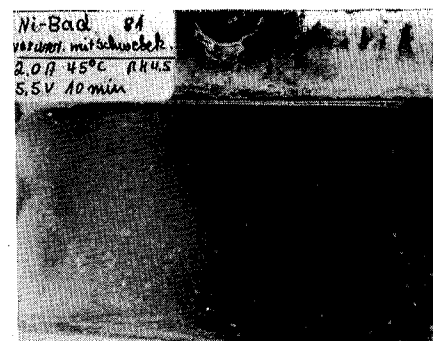
Fig. 62. Bright nickel plating bath (81)
Contaminated with solid impurities
in suspension
2.0 amp   45°C   pH 4.5   5.5 v   10 min
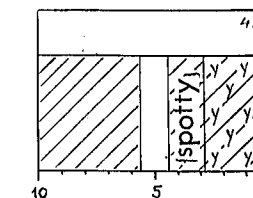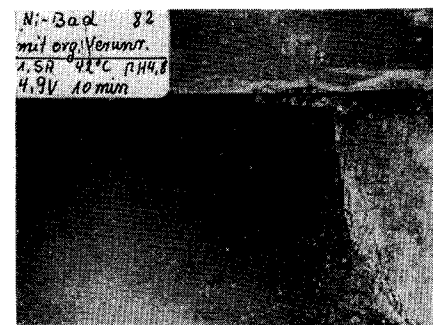
Fig. 63. Bright nickel plating bath (82)
With organic impurities
1.5 amp   42°C   pH 4.8   4.9 v   10 min
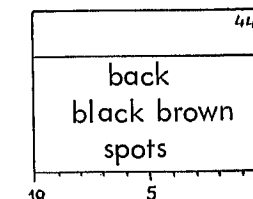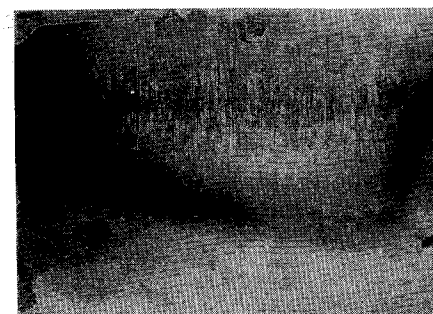
Fig. 64. Bright nickel plating bath (82)
With organic impurities
Reverse Side of Fig. 63
Dark brown stains
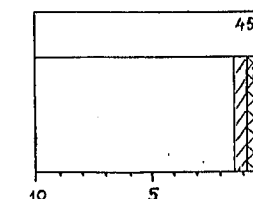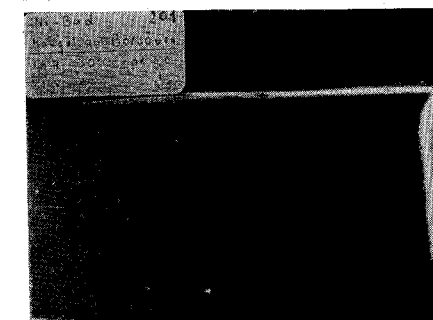
Fig. 65. Bright nickel plating bath (201)
Low boric acid concentration
1.9 amp   50°C   pH 4.0   5.1 v   10 min

CHAPTER 5

BRIGHTENERS IN NICKEL PLATING SOLUTIONS

THE INFLUENCE of brighteners in a nickel plating solution can only be clearly seen in the absence of impurities. For the purpose of these Hull cell tests, a matt nickel plating solution of the Watts type was made up and carefully purified as follows:

nickel sulphate	300 grams
nickel chloride	80 grams
boric acid (pure)	40 grams

were dissolved in approximately 800 ml hot water and brought to boiling. The pH was adjusted to pH 3·0 with dilute chemically pure sulphuric acid. A potassium permanganate solution was then added and the sample heated to 60°C to oxidise any oxidisable compounds present in the solution. This causes the electrolyte to turn a dirty green colour. Any excess of permanganate was then destroyed by adding hydrogen peroxide. The solution was then brought once more to boiling which destroys any excess hydrogen peroxide and clears the solution. As already described in the section on 'Iron Contamination' (p. 34) nickel carbonate was prepared with a small part of the solution and this was used to raise the pH to 6·4. After allowing the solution to stand for some time it was filtered and made up to 1 litre with distilled water. The solution was then adjusted to pH 4·5 with sulphuric acid and electrolysed at for 5 amp-hours using a corrugated cathode and stirring the solution. Subsequently the solution was filtered again. Fig. 66 shows a Hull cell panel from such a bath.

The following illustrations are designed to show the influence of brightener additions. In principle it is immaterial from which supply house the

Effect of Brighteners of Type II
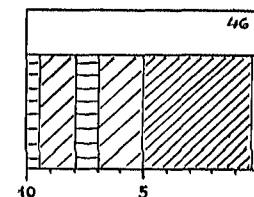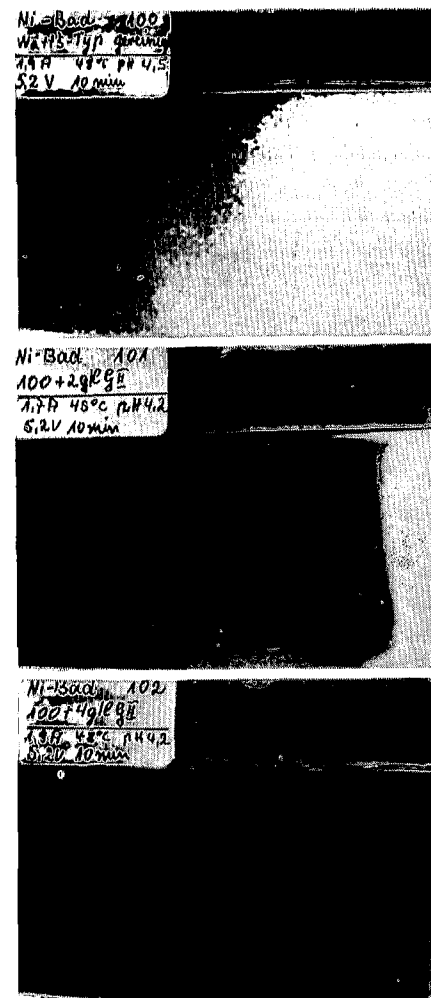
Fig. 66. Nickel plating bath (100)
Watts type, matt, purified
1.9 amp 48°C pH 4.5 5.2 v 10 min

Fig. 67. Nickel plating bath (101)
Soln (100) + 2 g/l B II
1.7 amp 45°C pH 4.2 5.2 v 10 min

Fig. 68. Nickel plating bath (102)
Soln (100) + 4 g/l B II
1.9 amp 48°C pH 4.2 5.2 v 10 min

brighteners have been obtained, the important distinction being between two types of brightener:

Brighteners of type I (abbreviated as B I). These produce the full brightness of the deposit and exert their effect mainly within the high current density range.

Brighteners of type II (abbreviated as B II). These widen the bright plating range particularly at low current density areas; they may also have other functions.

Modern bright plating solutions also frequently contain wetting agents and these too may have secondary effects.

B II in concentrations of 2 g/1 (Fig. 67) or 4 g/1 (Fig. 68) was added to the basic dull nickel electrolyte. The test panels show how with increasing concentration of this brightener the deposit is uniformly brightened in the low current density range. On the other hand the deposit in the high current density ranges remains matt. The strong effect of this brightener is seen in Fig. 68 which shows that very bright coatings are still obtained at current densities up to 100 amp/sq ft. This type of brightener is used in barrel plating, while in still plating it is mainly used for the achievement of semi-bright or satin finishes.

The action of Brightener I is shown in Figs. 69 to 72. As increasing concentrations of this brightener are added to the dull nickel bath, the deposit in the high current density areas becomes increasingly bright. This series of panels also shows that concentrations of the brightener below 2 g/1 are insufficient. At a concentration of 1 g/1 brightener the high current density area is still matt (see Fig. 69), at 1·5 g/1 the same current density range shows a satin finish (Fig. 70) while at 2 g/1 the whole panel is fully bright (see Fig. 71). As shown in Fig. 72, however, the presence of an excess of the brightener may be harmful ; this panel was plated in a solution containing 4 g/1 of this brightener. As the high current density end the deposit is brittle and exfoliates while the nickel fails to cover in the low current density area.

Effect of Brighteners of Type I
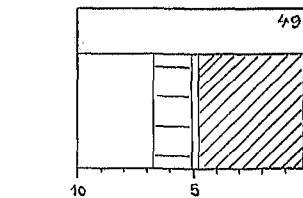
Fig. 69. Nickel plating bath (111)
Soln (100) + 1 g/l B I
2.0 amp   47°C   pH 4.2   5.2 v   10 min
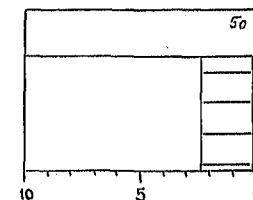
Fig. 70. Nickel plating bath (112)
Soln (100) + 1.5 g/l B I
1.9 amp   47°C   pH 4.2   5.2 v   10 min
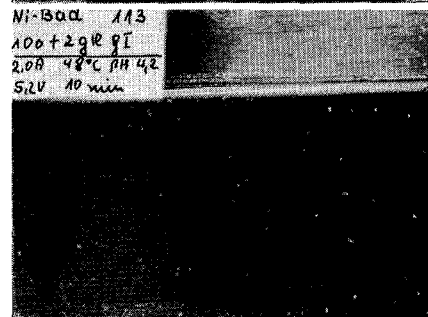
Fig. 71. Nickel plating bath (113)
Soln (100) + 2 g/l B II
2.0 amp   48°C   pH 4.2   5.2 v   10 min
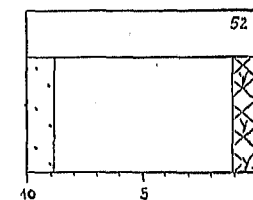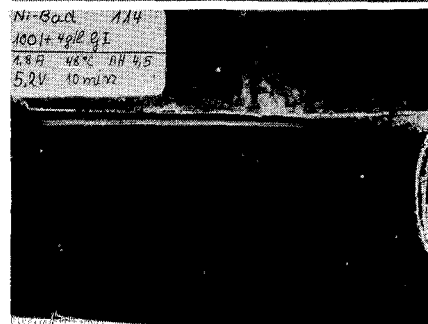
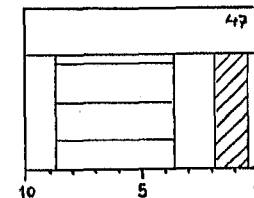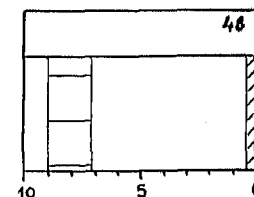Fig. 72. Nickel plating bath (114)
Soln (100) + 4 g/l B I
1.8 amp   48°C   pH 4.5   5.2 v   10 min

The combined effect of both the brighteners is shown in Figs. 73 to 78. Neither of the brighteners alone is sufficient to operate a fully bright nickel plating bath satisfactorily in continuous production. Only in combination do the brighteners give the required fully bright finish over the whole of the current density range. In the case of the panels shown in Figs. 73 to 75, the correct concentration of B II is 4 g/l. Fig. 73 shows the panel plated in a solution of low B I content; this shows a shadow in the high current density range. Fig. 74 shows an electrolyte with the correct B I concentration, while Fig. 75 illustrates a panel plated in a solution containing an excess concentration of B I.

It may also happen that while the correct concentration of B I is present, the solution may contain too little B II (see Fig. 76). In this case the bright throwing power of the bath is poor. The deposits in the low and medium ranges of current density are covered with a bloom. Fig. 77 is similar to Fig. 74 as here the correct concentration of B I is supplemented with the right B II concentration. At the same time this illustration shows that the Hull cell panels invariably show the same condition of the electrolyte in the same way, irrespective of the series of operations in which this condition has been arrived at. It is this fact which makes it possible to use the Hull cell to correct the composition of the solution. Fig. 78 shows the effect of an excess of B II. As distinct from an excess of B I an excess of B II causes no visible effects.

Once the influence of the brighteners of any specific bright plating solution has been investigated, it is not difficult to estimate their concentrations in the solution from the patterns produced on the Hull cell panels.

Care must be taken, however, not to draw the wrong conclusions from the appearance of the panels. An example is the apparent similarity of Fig. 43 to Fig. 76. The first panel shows the effect of contamination with manganese and iron while the second shows the result of lack of Brightener II. The difference can be determined simply by adding B II to the sample of the solution. If the shadow disappears, it is clear that the fault was due to insufficient B II concentration. The control experiment is therefore an important feature of the use of the Hull cell and the correct interpretation of the results. This applies particularly when the solution is an unfamiliar one. As mentioned above moreover, it is important to make up a fresh solution sample for each test.

Combined Effect of Both Brighteners
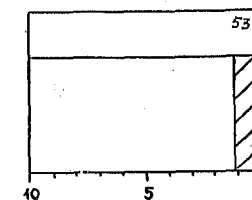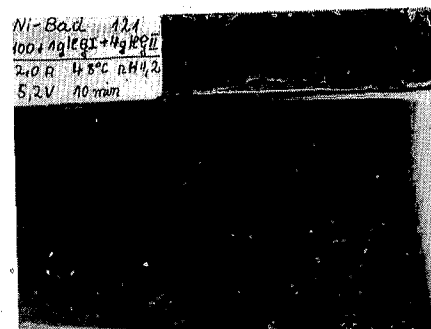
Fig. 73. Nickel plating bath (121)
Soln (100) + 1 g/l B I + 4 g/l B II
2.0 amp 48°C pH 4.2 5.2 v 10 min
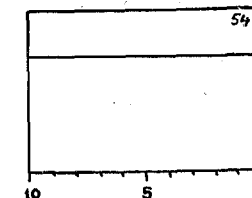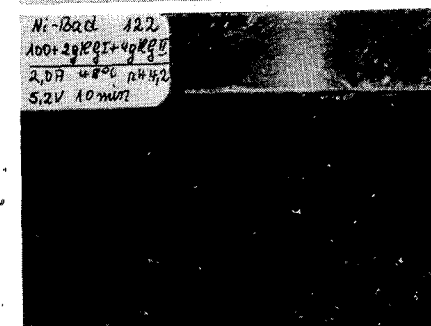
Fig. 74. Nickel plating bath (122)
Soln (100) + 2 g/l B I + 4 g/l B II
2.0 amp 48°C pH 4.2 5.2 v 10 min
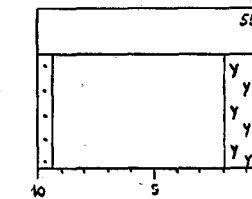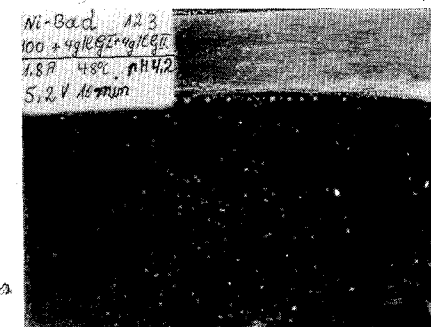
Fig. 75. Nickel plating bath (123)
Soln (100) + 4 g/l B I + 4 g/l B II
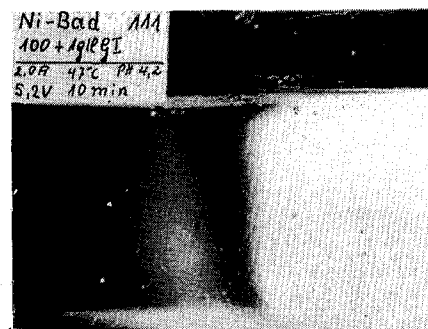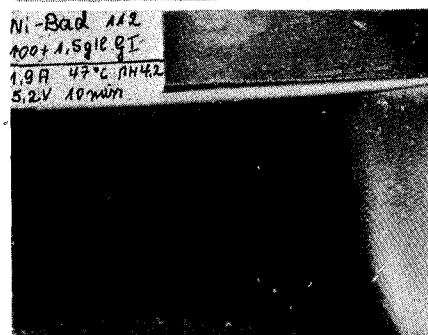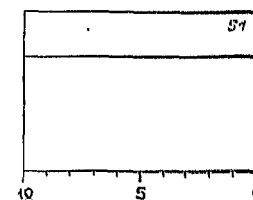1.8 amp 46°C pH 4.2 5.2 v 10 min
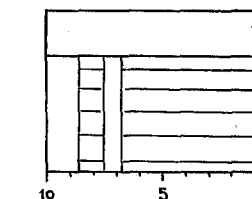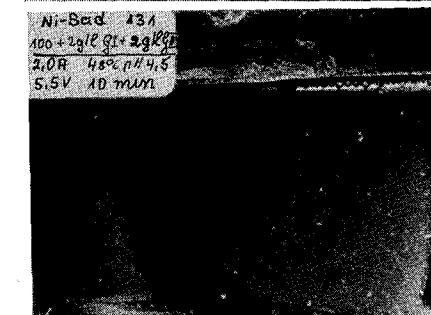
Fig. 76. Nickel plating bath (131)
Soln (100) + 2 g/l B I + 2 g/l B II
2.0 amp 48°C pH 4.5 5.5 v 10 min

Both Brighteners (continued)
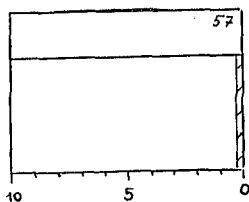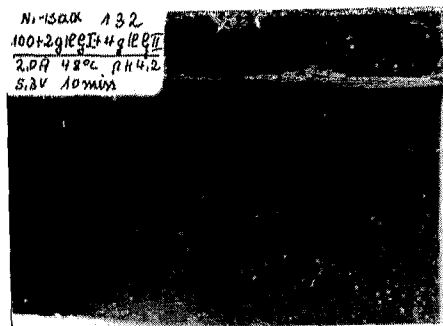
Fig. 77. Nickel plating bath (132)
Soln (100) + 2 g/l B I + 4 g/l B II
2.0 amp   48°C   pH 4.2   5.3 v   10 min
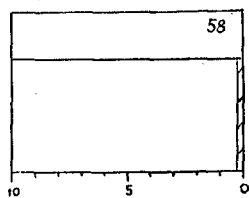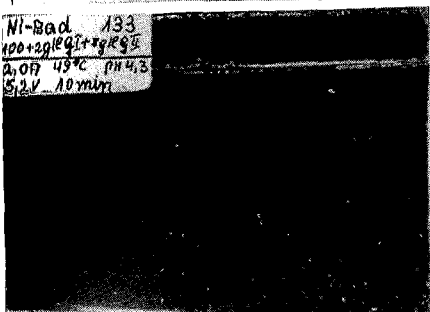
Fig. 78. Nickel plating bath (133)
Soln (100) + 2 g/l B I + 8 g/l B II
2.0 amp   49°C   pH 4.3   5.2 v   10 min

Fig. 78a illustrates the difference in Hull cell test patterns between a fully-bright and a semi-bright nickel plating solution, in this case solutions of W. Canning & Co. Ltd., Birmingham, while Fig. 78b demonstrates the effect of brightener breakdown products.

80	50	30	20 12	6	2	amp/ft2
8·6	5·4	3·2	2·2 1·3	0·6 0·2		amp/dm2
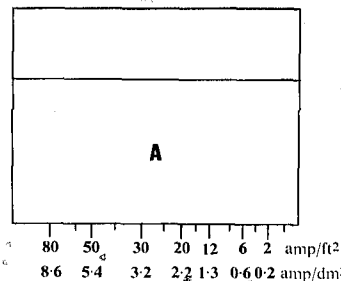
Current 2 amperes   Time 10 minutes
Nisol Bright Nickel Solution

80	50	30	20 12	6	2	amp/ft2
8·6	5·4	3·2	2·2 1·3	0·6 0·2		amp/dm2
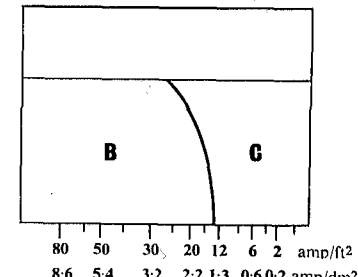
Current 2 amperes   Time 10 minutes
Surfol Semi-bright Nickel Solution

Fig. 78a. Illustrating the difference in Hull cell test patterns between a fully-bright and a semi-bright nickel plating solution (solutions of W. Canning & Co. Ltd., Birmingham).

New Surfol solution

Solution containing 1·6 fl oz/gal (10 g/l) breakdown products

| amp/ft² | 40 25 15 10 6 31 |
| amp/dm² | 4·3 2·7 1·6 1·1 0·6 0·3·0·1 |
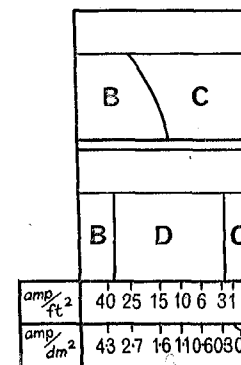
Fig. 78b. Demonstrating the effect of brightener breakdown products on Hull cell test panels. (Surfol semi-bright nickel plating solution of W. Canning & Co. Ltd.; panels plated at 1 amp for 15 minutes).

Key: A - Bright, B - Hazy Bright, C - Semi-bright, D - Dull, E - Burnt.

CHAPTER 6

CADMIUM PLATING SOLUTIONS

T H E   M O S T widely used cadmium plating solutions are based on cyanides. The metal content of such solutions is normally between 10 and 40 g/l cadmium and current densities are usually between 5 and 50 amp/sq ft. It is seen from the diagram in Fig. 18 that the best total Hull cell current for the current density ranges which come into consideration is 1·0 ampere. Before giving examples for the testing of cadmium plating baths, it is useful to discuss the terminology of the cyanide concentration.

In the cadmium cyanide solution, the cadmium is present as a complex with the cyanide. The cadmium compounds known as cadmium plating salts are formed according to the following equations:

$$Cd^{++} + 2(CN)^- = Cd(CN)_2 \text{ cadmium cyanide} \tag{7}$$

$$Cd^{++} + 3(CN)^- = [Cd(CN)_3]^- \text{ tricyanocadmiate ion} \tag{8}$$

$$Cd^{++} + 4(CN)^- = [Cd(CN)_4]^- \text{ tetracyanocadmiate ion} \tag{9}$$
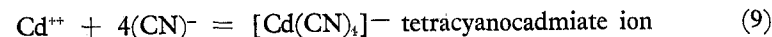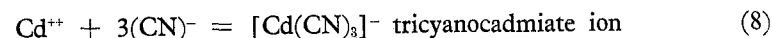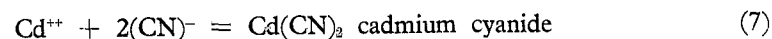
Which of the last two complexes exists in the cadmium plating bath or whether they both exist side by side is not yet clear. Due to the fact that both of these complexes are dissociated to a considerably higher degree than, e.g., the corresponding copper complexes, it is not possible to refer to a 'free' cyanide concentration in the case of the cadmium plating solution. For instance, while according to equation (8) 39·3 g sodium cyanide should be sufficient to convert 30 g cadmium to the $Na[Cd(CN)_3]$ complex, the author has found that, starting with cadmium oxide, hydroxide or carbonate, 65 g sodium cyanide were required in each case. This would correspond to the equation:

$$Cd^{++} + 5(CN)^- = [Cd(CN)_3]^- + 2(CN)^- \tag{10a}$$

$$\text{or} \quad = [Cd(CN)_4]^{--} + (CN)^- \tag{10b}$$
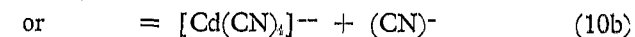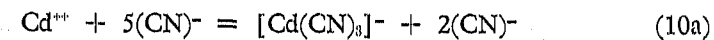
In order to avoid the difficulties of the 'free' cyanide concentration only the total cyanide content of the solution will be referred to in this chapter, which describes the total sodium cyanide concentration of the plating bath. As there are no uniform bath types which can be distinguished among cadmium plating solutions, the cadmium plating bath will be used to provide an example of the investigation of the operating conditions of a plating solution. The same factors will also apply to the testing of cadmium plating baths of different compositions in the Hull cell. It is not possible to reproduce all the panels which were prepared in this series of experiments and therefore only the most important are included.

Hull cell operating conditions

Cathode: brass sheet (Ms 72) bright rolled, degreased with Vienna lime, dipped in hydrochloric acid and rinsed. After the conclusion of the test the cathode was rinsed, dipped for approx 2 seconds in 0·25 per cent sulphuric acid, rinsed and dried.

Anode: Cadmium anode, 4 mm thick, perforated with 4 mm diameter holes.

Current: The total current through the Hull cell was 1·0 amp for the duration of the test. In some cases this required control during electrolysis. The voltage given is that required at the end of the period.

Temperature: 22 to 26°C.

Time of plating: 3 minutes.

Agitation: As required, by stirrer.

The best conditions for the test were first determined in a preliminary series of experiments. When the solution was stirred mechanically in the Hull cell undesirable flow phenomena were reproduced on some panels, depending on the plating conditions. Figs. 79 and 80 show panels produced in the same electrolyte with and without agitation respectively. Moving the solution in front of the anode produced excessive voltage fluctuations in some instances. Agitated electrolytes required lower voltages. The author found no significant differences between the use of plain and perforated anodes but all the experiments were carried out with the same type of anode for the sake of uniformity. The anode was activated before each experiment in order to obtain a clean metallic surface which would not give false readings for the cell voltage.

The plating conditions for the panels shown in the photographs are listed in Table 1.

Test results

15 and 30 grammes cadmium as cadmium carbonate were dissolved in the required amount of sodium cyanide solution and tested in the Hull cell. In order to avoid excessive anode polarization the cell was agitated by mechanical stirring throughout these tests. Figs. 81 and 82 show the results for 15 and 30 g/l cadmium respectively. Fig. 81 shows a broken and perforated coating in the low current density range. As the metal concentration increases, the voltage drops.

Table 1. Solution composition and Hull cell operating conditions for the panels reproduced in Figs. 79 - 100

Fig. No.	Cd g/l	NaCN (total) g/l	Na_2CO_3 g/l	brightener g/l	temp °C	time min	current amps	voltage volts	agitation
81	15	65	15	—	25.7	3	1.0	5.4	yes
82	30	130	30	—	24.0	3	1.0	2.7	yes
83	15	90	15	—	24.5	3	1.0	4.1	no
84	30	180	30	—	25.6	3	1.0	1.9	no
85	15	65	15	—	24.0	3	0.6	>6.0	no
86	15	85	15	—	24.5	3	1.0	4.1	no
87	15	115	15	—	24.5	3	1.0	3.2	no
88	15	163	15	—	24.5	3	1.0	2.3	no
89	15	115	15	2.5	24.0	3	1.0	3.0	no
90	15	115	15	5	23.8	3	1.0	3.0	no
91	15	115	15	10	23.8	3	1.0	2.9	no
92	15	115	15	20	23.8	3	1.0	3.0	no
93	30	170	30	20	22.0	3	1.0	2.2	no
94	25	142	25	16.7	22.0	3	1.0	2.3	no
95	21.5	122	21.5	14.3	22.0	3	1.0	2.4	no
96	19	107	19	12.5	22.0	3	1.0	2.6	no
97	15	65	15	10	25.7	3	1.0	5.3	yes
98	15	87	15	10	25.7	3	1.0	2.85	yes
99	15	109	15	10	25.7	3	1.0	2.05	yes
100	15	131	15	10	25.7	3	1.0	1.8	yes
79	15	165	15	—	25.7	3	1.0	1.8	yes
80	15	165	15	—	23.5	3	1.0	1.7	yes

Influence of Agitation

See Table 1 for details

Fig. 79. With agitation.
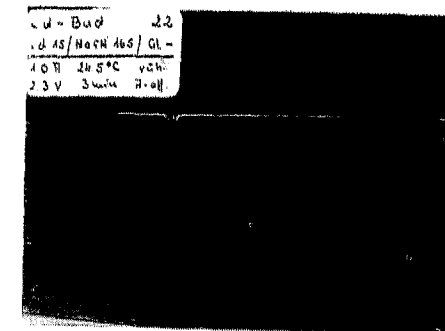
Fig. 80. Without agitation.
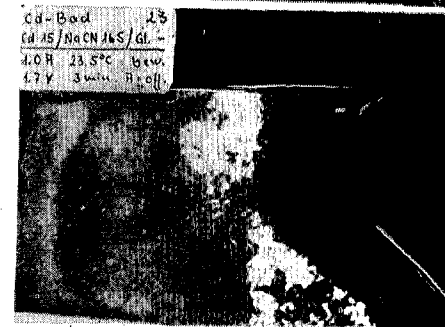
Fig. 81. With agitation.
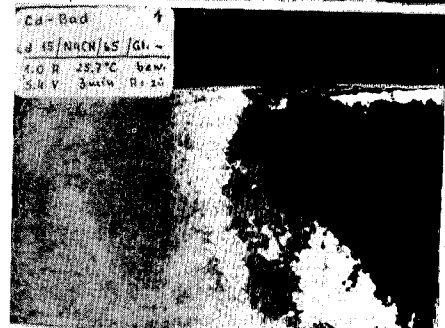
Fig. 82. Without agitation.
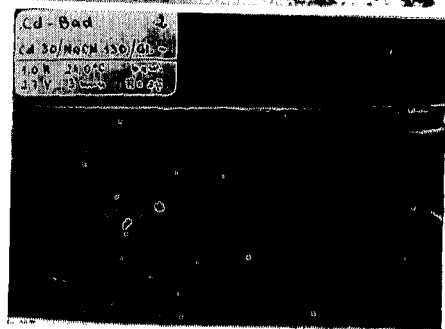
Cadmium and cyanide contents

The object of the next series of experiments was to determine the behaviour of the plating solution after adding the same proportion of sodium cyanide. In the first two experiments, the Cd : NaCN ratio was made up to 1 : 6 in both cases while the cadmium content was kept at 15 g/l and 30 g/l respectively (see Figs. 83 and 84). The panels showed that in this case, as in Fig. 82, the low current density range is covered better by the solution with the higher metal concentration. No agitation was required for these two panels. Figs. 81 to 84 together show that as the metal concentration is increased and at constant Cd : NaCN ratio, the covering power of the bath improves and the cell voltage decreases.

Solution Concentration

See also Figs. 93 - 96, p. 64
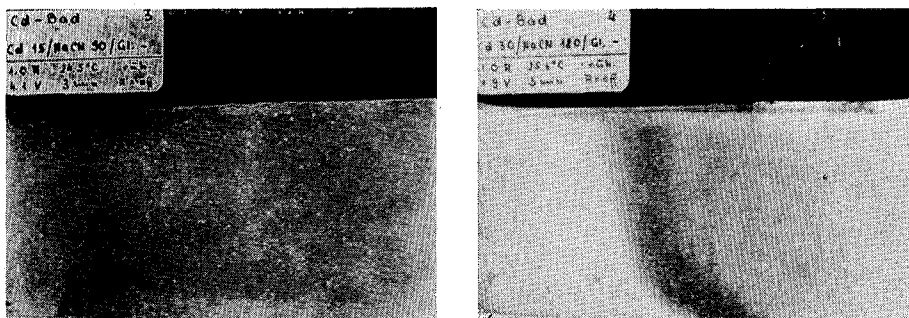
Figs. 83 and 84. The solution of Fig. 84 (right) was the more concentrated. See Table 1 (p. 58) for details.

The next series of tests showed the influence of increasing the sodium cyanide concentration in solution with the same metal content. In general this resulted in an improvement in covering power of the bath. This can be seen most clearly on the reverse sides of the panels. It is necessary to ensure that the panels are in the same relative position to the cell wall, particularly in the tests in which the deposits on the back of the panels are important. The improvement in the covering power is shown in Figs. 85 to 88. At the same time the bath voltage decreases. As the cyanide concentration increases the rate of gas evolution increases and becomes noticeable in the low current density areas. Naturally the more vigorous the gas evolution, the poorer the cathode efficiency of the operation.

Effect of Increasing Cyanide Concentration

See also Figs. 97 - 100, p. 65

For details see Table 1 page 58

Fig. 85
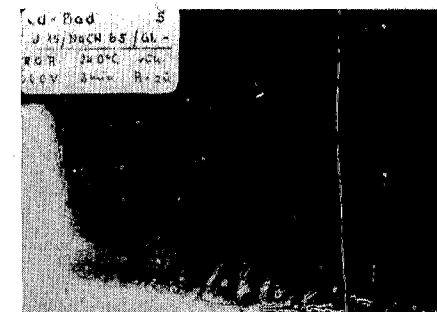
Fig. 86
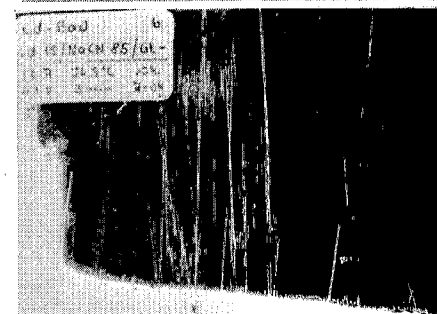
Fig. 87
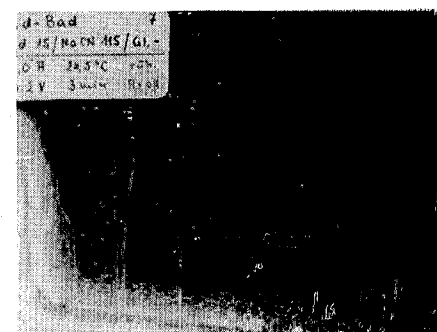
Fig. 88
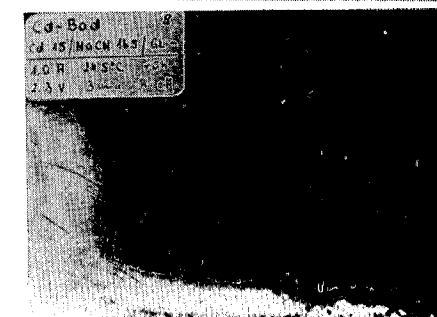
From the foregoing experiments it may be concluded that

1. At a cadmium : sodium cyanide ratio less than 1 : 5:
   a) the covering power is poor,
   b) the voltage fluctuates due to anode polarization,
   c) gas evolution is slight and the cathode efficiency is high.

2. At a cadmium : sodium cyanide ratio of 1 : 6:
   a) covering power is good,
   b) voltage fluctuations are slight,
   c) gas evolution is normal.

3. At a cadmium : sodium cyanide ratio above 1 : 7:
   a) covering power is good,
   b) the voltage remains constant,
   c) there is strong gas evolution.

These observations are summarised in Table 2.

Table 2. Effect of cadmium and cyanide contents

| | Approximate bath voltage | | | |
Gas evolution	1·5 - 2·0	2·0 - 3·0	3·0 - 4·5	Condition of the anode
weak	Cd very high NaCN too low	Cd high NaCN too low	Cd medium NaCN too low	passive
normal	Cd high NaCN normal	Cd medium NaCN normal	Cd low NaCN normal	lightly filmed
vigorous	Cd medium NaCN too high	Cd low NaCN too high	Cd very low NaCN too high	clean

Explanation :

Cd very high	over 40 g/l
high	30 - 40 g/l
medium	15 - 30 g/l
low	10 - 15 g/l
very low	below 10 g/l

Brightener concentration

In tests on the influence of brighteners, the Cd : NaCN ratio was held constant and increasing amounts of brightener were added to the solution. The effect of these additions is seen in Figs. 89 to 92. When the brightener concentration was below 2·5 g/l the range within which bright deposits are obtained lay below 10 amp/sq ft (see Fig. 89). The bright range extended to 10 amp/sq ft at a brightener concentration of 5 g/l (see Fig. 90) and covered the range between 75 and 20 amp/sq ft at 10 g/l brightener. Finally, in the presence of 20 g/l brightener the bright range was between 75 and 25 amp/sq ft. All these panels were plated in solutions containing an excess of 25 g/l sodium cyanide. The streaks caused by gas evolution can be seen clearly in these illustrations. In all four of the experiments the voltage was the same.

Effect of Increasing Brightener Concentration

Fig. 89
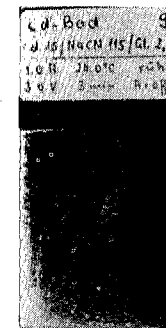
Fig. 90
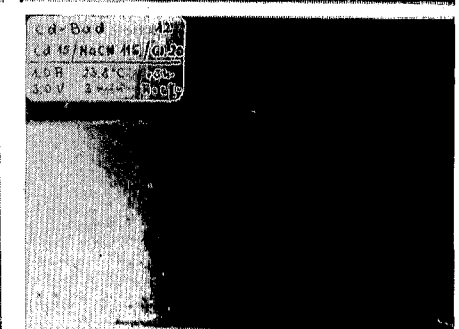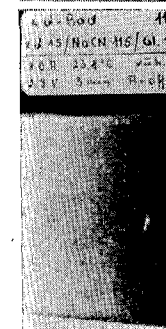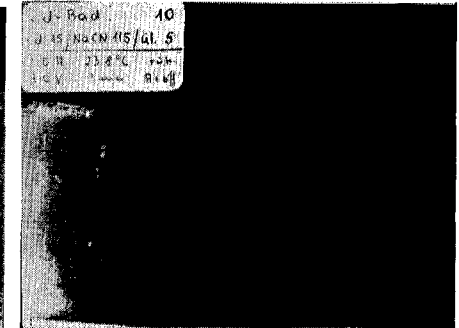
Fig. 91

Fig. 92

Demonstrating effect of increasing brightener concentration.
See Table 1, p. 58 for details.

In the next experiments the basic electrolyte was diluted in stages. Here it was seen that as the total concentration of the plating solution decreases, the bright plating range is shifted to lower current densities (see Figs. 93 to 96). At the same time the bath voltage rises.

Solution Concentration

See also Figs. 83 and 84, p. 60

Fig. 93
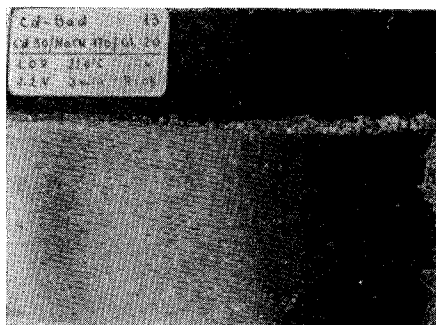
Fig. 94
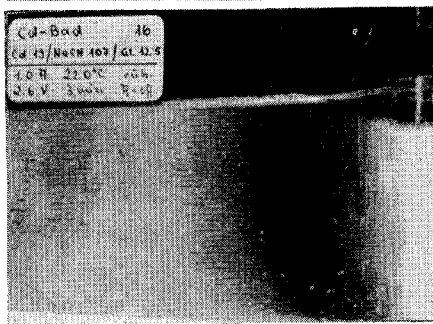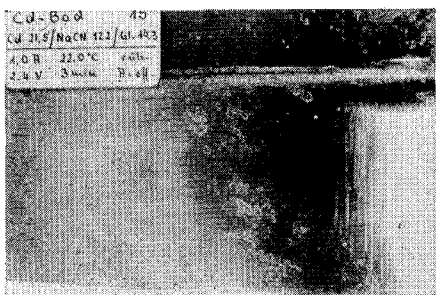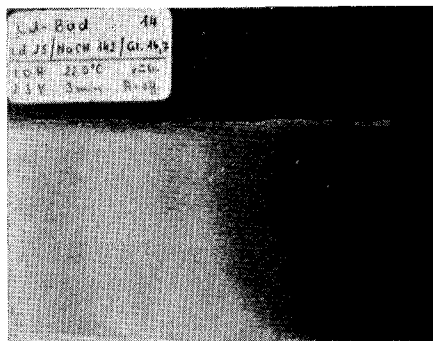
Fig. 95

Fig. 96

Demonstrating the effect of diminishing total concentration.
See Table 1, p. 58 for details.

If both the cadmium metal and brightener concentrations are held constant and the sodium cyanide concentration of the solution is raised, the bright plating range is shifted to higher current densities as shown in Figs. 97 to 100. At the same time the matt streaks in the low current density areas disappear in favour of an almost uniform satin finish. These panels were plated under conditions of agitation to facilitate observation of the voltage changes. They also show replicas of flow phenomena.

Cyanide Concentration

See also Figs. 85 - 87, p. 61

Fig. 97
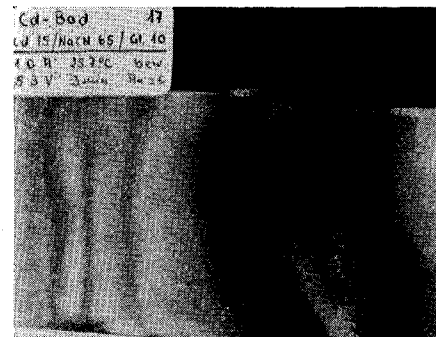
Fig. 98
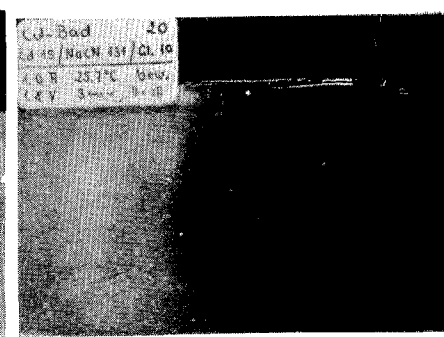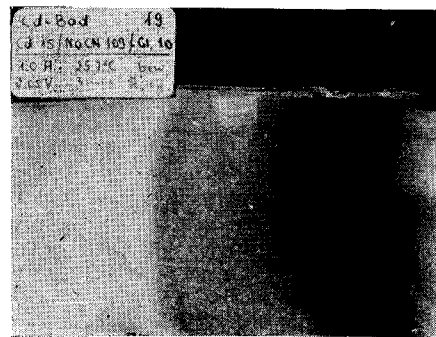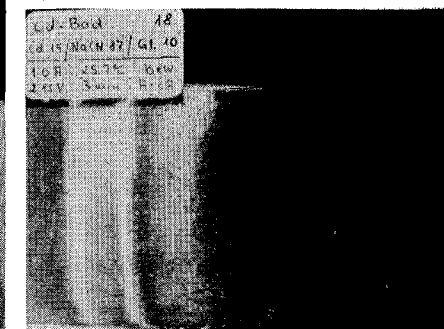
Fig. 99

Fig. 100

Effect of increasing total cyanide concentration.
See Table 1, p. 58 for details.

Finally a panel is shown (see Fig. 101) on which the effect of gas evolution is clearly visible. The deposit on this panel has a similar appearance to a bright nickel deposit obtained from a solution contaminated with zinc. As distinct from the latter, however, and contrary to appearances, the deposit is not brittle. For this illustration the lighting was reversed and the bright areas appear white.

Effect of Gas Evolution

Fig. 101. Effect of gas evolution.

Caustic soda

The author also investigated the influence of additions of caustic soda to the cadmium plating bath. These tests showed that with increasing caustic soda content the voltage decreases and with additions of up to 10 g/l there is a widening of the bright plating range. In these experiments the sodium carbonate concentration was roughly equivalent to the cadmium content of the solution as the latter was prepared from freshly precipitated cadmium carbonate, which produces approximately 106 g sodium carbonate for 112 g cadmium.

Solution composition

The experiments described above show that the effect of the main constituents of the cadmium cyanide plating bath are not independent of each other and similar results may have different causes. The best results are achieved by determining the operating ranges at different cadmium and cyanide concentrations for each newly prepared cadmium plating solution. Fig. 102 shows the operating ranges for a dull cadmium plating bath as a function of the cadmium metal and sodium cyanide concentrations. The cadmium and sodium cyanide contents could be determined approximately by means of two Hull cell tests. For this purpose the voltage of the cell is determined at 1·0 ampere. In the second experiment 7·5 g corresponding to 30 g/l) sodium cyanide are added and the voltage is determined once more at the same current. The position of the cadmium curve in the diagram in Fig. 102 has been obtained by this method. It is then only necessary to compare the slope of the curve corresponding to the cadmium concentration. The author has had excellent experiences with this diagram which has replaced the analytical determination of the solution composition.
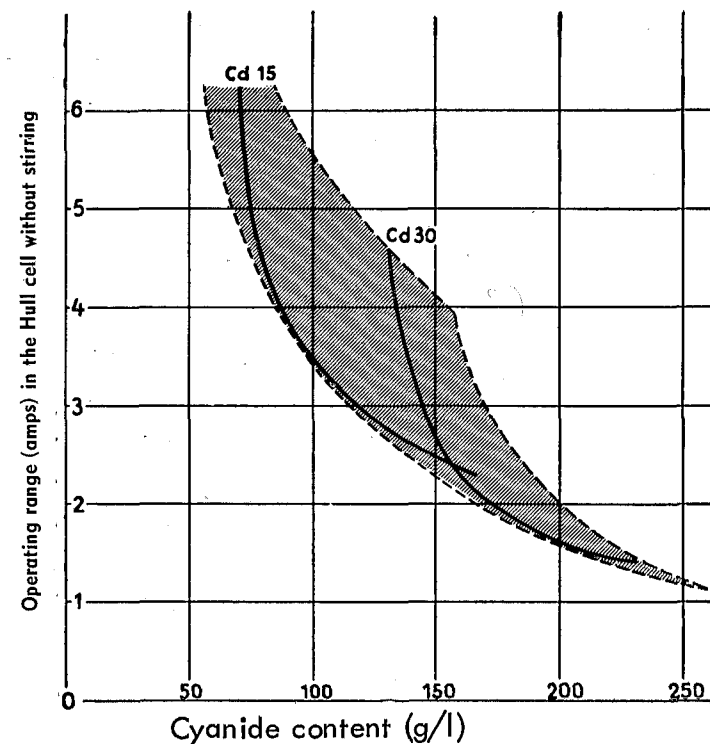
Fig. 102. Operating ranges for a dull cadmium bath.

CHAPTER 7

ZINC PLATING SOLUTIONS

A s I n the case of cadmium the cyanide zinc plating bath is used far more frequently than the acid solution. The author has had no special experience with zinc plating solutions and set himself the task of investigating the operating conditions of these solutions by means of Hull cell tests. The results were highly interesting and may serve as an example of the way in which the Hull cell may be used to accustom oneself to working with unfamiliar plating solutions.

The object was to determine the solution composition at which fine-grained zinc coatings are deposited at room temperature with good covering properties and at good current efficiencies. It is known that the main constituents of the cyanide zinc solution are zinc cyanide or zinc oxide, sodium cyanide and sodium hydroxide with the addition of sulphide as purifying agent. The zinc concentration in these experiments was 35 ± 5 g/l.

The dissolution of zinc cyanide or zinc oxide in solutions of sodium cyanide or caustic soda is normally expressed by the following equations:

$$Zn(CN)_2 + 2NaCN = Na_2[Zn(CN)_4] \qquad (11)$$
$$Zn(CN)_2 + 4NaOH = Na_2[Zn(OH)_4] + 2NaCN \qquad (12)$$

or

$$Zn(CN)_2 + 2NaOH = \tfrac{1}{2}Na_2[Zn(OH)_4] + \tfrac{1}{2}Na_2[Zn(CN)_4] \qquad (13)$$
$$ZnO + 4NaCN + H_2O = Na_2[Zn(CN)_4] + 2NaOH \qquad (14)$$

or

$$ZnO + 2NaCN + H_2O = \tfrac{1}{2}Na_2[Zn(CN)_4] + \tfrac{1}{2}Na_2[Zn(OH)_4] \qquad (15)$$
$$ZnO + 2NaOH + H_2O = Na_2[Zn(OH)_4] \qquad (16)$$
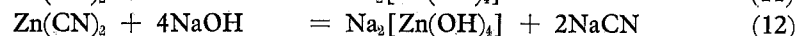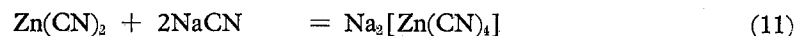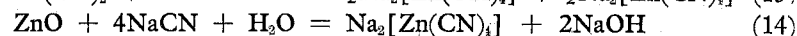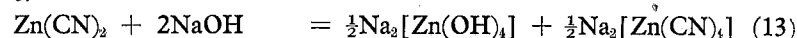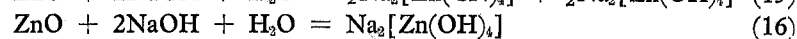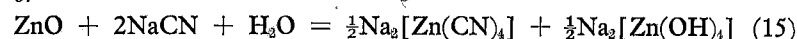
Experiments carried out by dissolving the chemicals established however that only Equation 11 corresponds to the facts. None of the other dissolution experiments resulted in whole number stoichiometric factors even if it is assumed that instead of four complex ions only three are combined with the zinc atom. Accordingly the author has calculated all the (CN) groups present as NaCN and all the (OH) groups in the solution as well as the 2 OH groups which are formed by the dissolution of 1 gram molecule of zinc oxide, as NaOH.

As discussed in the chapter on cadmium plating solutions, it is not possible to describe the zinc solution in terms of its 'free' cyanide concentration. The amounts of cyanide which are actually required to dissolve the metal are seen in the diagrams reproduced in Figs. 103 and 104. Electrolytes were then prepared to cover as wide a range as possible of the Zn-NaCN-NaOH system by combining solutions prepared in these experiments and with the addition of sodium polysulphide. The solutions in Fig. 103 contain 20 g/l zinc, while those in Fig. 104 contain 35 g/l zinc. Only the experiments carried out with the more concentrated solution shown in Fig. 104 will be described here.
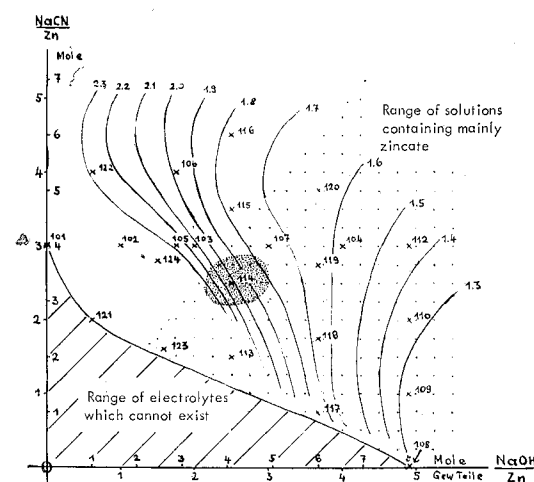
Fig. 103. Range of zinc plating solutions containing 20 g/l zinc and ranges of constant voltage in the Hull cell at 20°C, 1 amp (total cell current), without agitation.
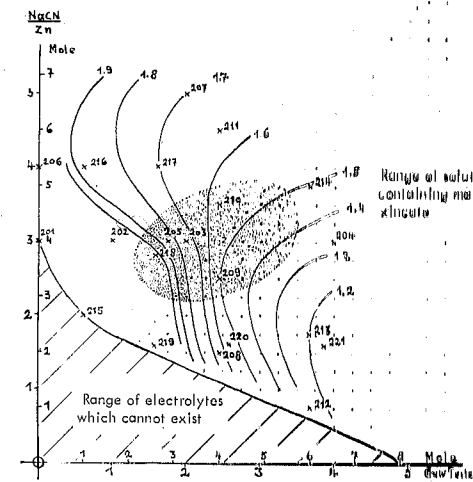
Fig. 104. Range of zinc plating solutions containing 35 g/l zinc and ranges of constant voltage in the Hull cell at 20°C, 1 amp (total cell current), without agitation.

Test conditions

The experimental data are reproduced in Table 3.

The other operating conditions were as follows:

Cathode: Brass sheet, Ms 72, bright rolled, degreased with Vienna lime, dipped in hydrochloric acid and rinsed. After the test the panel was rinsed thoroughly and half of the area of the panel used for evaluation was dipped in 0·25 per cent nitric acid. This removed the dark film and improved the features of the panel.

Anode: Zinc anode, 99·99 per cent zinc, not perforated.

Current: With few exceptions all the tests were performed at a cell current of 1·0 amps. Where possible or necessary the current was adjusted during the test. The voltage given is the bath voltage at the end of the test.

Temperature: 20 ± 1°C.

Time of test: 5 minutes.

Agitation: None.

Table 3. Experimental data for Hull cell tests on zinc plating solutions

Fig. no.		Zn g/l	Ratio of constituents in pts by wt			Temp °C	Time min	Amps	Volts	Gas† evolution	Anode remarks
Front	Back		Zn	NaCN	NaOH						
105	106	35	1	3	0	20.5	5	0.05	>6.0	—	l.f.
107	111	35	1	3	1	20.3	5	1.0	2.35	5	f.
109	113	35	1	3	2	20.3	5	1.0	1.75	4	f.
110	114	35	1	3	4	20.0	5	1.0	1.58	2	f.
126	130	35	1	3	4	20.0	5	1.0	1.58	2	f.
108	112	35	1	3	1.75	19.2	5	1.0	1.85	5	f.
115	118	35	1	4	0	20.5	5	0.72	5.0	(10)	c.
121	—	35	1	5	2	20.7	5	1.0	1.7	10	f.
132	136	35	1	1.5	2.45	20.3	5	1.0	1.6	0.5	l.f.
133	137	35	1	2.5	2.45	20.0	5	1.0	1.5	2	f.
134	138	35	1	3.5	2.45	20.0	5	1.0	1.55	4	f.
135	139	35	1	4.5	2.45	20.0	5	1.0	1.65	8	l.f.
122	—	35	1	4.5	2.45	20.0	5	1.0	1.65	8	l.f.
124	128	35	1	0.75	3.67	20.0	5	1.0	1.25	0	l.f.
125	129	35	1	1.75	3,67	20.0	5	1.0	1.2	0	l.f.
127	131	35	1	3.75	3.67	19.8	5	1.0	1.5	6	l.f.
140	141	35	1	2	0.61	20.3	5	1.0	5.8	2	black
116	119	35	1	4	0.61	20.6	5	1.0	1.85	10	l.f.
117	120	35	1	4	1.61	20.7	5	1.0	1.7	10	l.f.
123	—	20	1	0	4.9	20.0	5	1.0	1.3	0	f.
142	—	31	1	3	2.0	20.0	5	1.0	1.67	2.5	f.
143	—	31	1	3	2.5	25.0	5	1.0	1.5	2.5	f.
144	—	31	1	3	2.5	30.0	5	1.0	1.37	1	s.f.
145	—	31	1	3	2.5	38.0	5	1.0	1.15	0	s.f.
146	—	31	1	3	2.5	33.5	5	2.0	2.35	3	black
147	—	31	1	3	2.5	30.8	5	1.0	1.35	0.5	black (a)
148	—	31	1	3	2.5	20.0	5	1.0	1.4	2	c. (b)
149	—	31	1	3	2.5	19.5	5	1.0	1.7	2.5	l.f. (c)
150	—	31	1	3	2.5	19.5	5	1.0	1.6	10	black (d)
151	—	31	1	3	2.5	20.0	5	1.0	1.25	0	l.f. (e)
152	—	31	1	3	2.5	21.0	5	1.0	1.45	0	black (f)

Key : l.f. lightly filmed
　　　f. filmed
　　　s.f. strongly filmed
　　　c. clear

† Arbitrary scale:
　　0 = no gassing
　　10 = very strong gassing

(a) With the addition of approx 1 g/l Cu.
(b) In the presence of chromate.
(c) With the addition of approx 2 g/l Cd.
(d) With the addition of approx 2 g/l Ni.
(e) With the addition of a little silver plating solution.
(f) Plus 0.11 g/l Ag*.

Effect of increasing hydroxide content

Starting with the sodium tetracyanozincate solution prepared according to equation 11 (Figs. 105 and 106), increasing amounts of sodium hydroxide were added to the electrolyte. The amounts added were 1 part by weight (Fig. 107), 1·75 parts by weight (Fig. 108), 2 parts by weight (Fig. 109) and 4 parts by weight (Fig. 110). The reverse of these panels is shown in Figs. 111 to 114.

Basic Solution

Panel front face   Panel back face
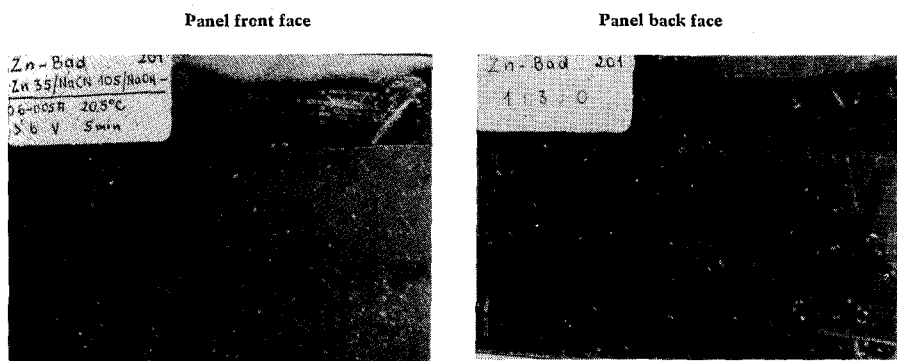
Figs. 105 and 106. Basic cyanide zinc plating solution. Fig. 106 shows the reverse face of Fig. 105. For details, see Table 3, p. 71.

The current of 1 amp through the Hull cell could not be maintained in the pure sodium tetracyanozincate solution. Zinc deposition was very slow, as is shown very clearly in Fig. 106 and the deposit was strongly attacked by the very dilute nitric acid solution. For the most part the experiment produced only the electrolytic decomposition of water, with a little co-deposited zinc. In the tests carried out with solutions with increasing sodium hydroxide concentration the conductivity of the electrolyte rose and the gas evolution became slower. However, the change in the deposit due to the change in the bath composition was hardly noticeable on the front of the panels.

The reverse of the panels show the results more clearly. Covering power was not significantly changed, as seen from the extent to which the area was covered by zinc. On the other hand the white U-shaped strip of coarsely crystalline zinc deposit was enlarged as the sodium hydroxide concentration increased. Only the transition areas were brightened by the nitric acid solution.

Increasing Hydroxide Concentration

Front face   Back face

Front face   Back face
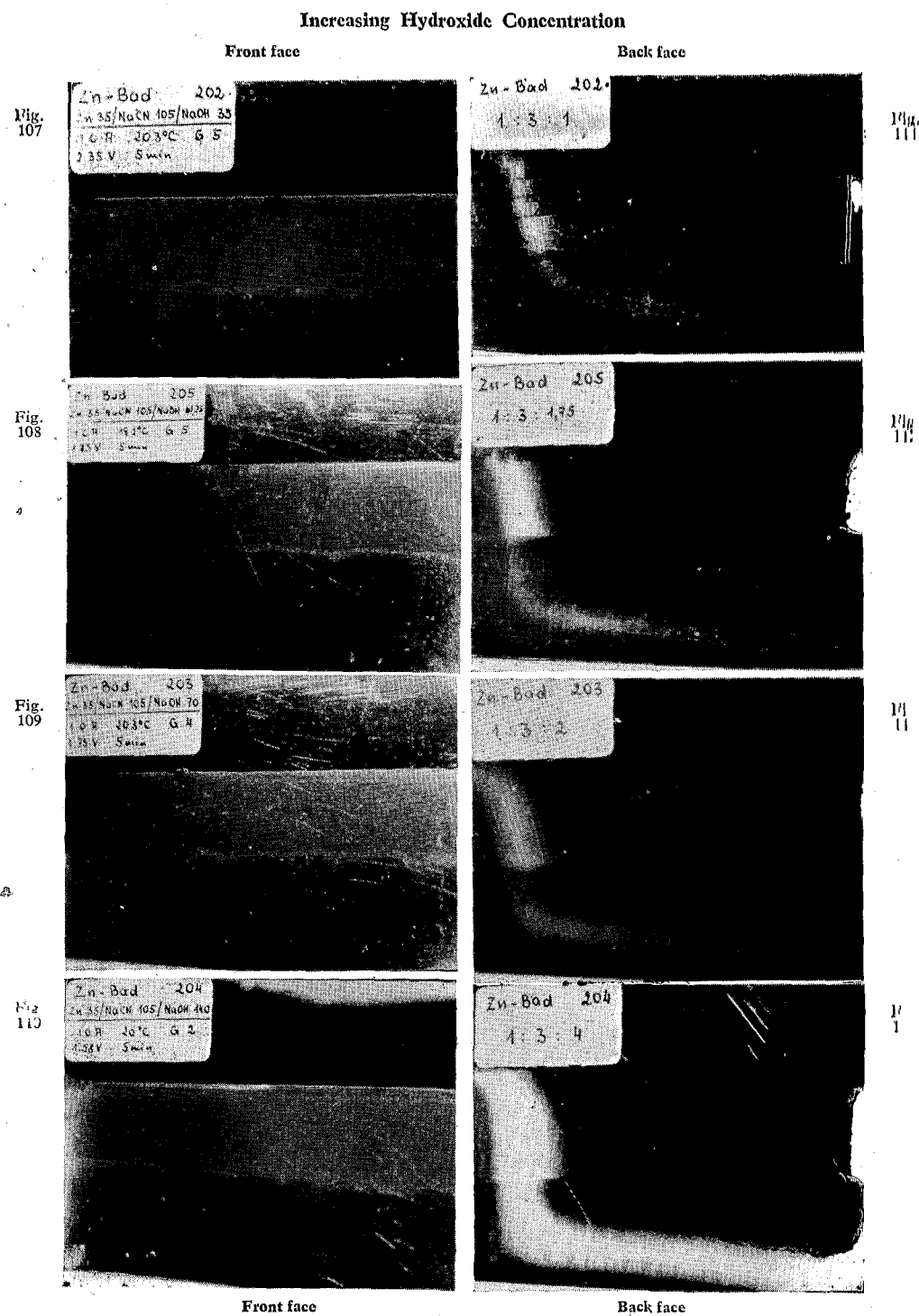
For details, see Table 3, p. 71

The following conclusions can be drawn from these observations:

At a constant Zn : NaCN ratio in the solution and with increasing sodium hydroxide content:

1. the conductivity increases as the voltage drops,
2. the cathode efficiency increases as the gas evolution diminishes,
3. the covering power is unchanged, and
4. the crystal structure of the deposit becomes coarser in the low current density areas.

Effect of increasing cyanide content

The Zn : NaCN ratio of the zinc plating bath expressed in parts by weight is called the ' M number '. For the solutions referred to in Figs. 105 to 114 the value is 3·0.

If the M number is increased to 4·0 (Figs. 115 - 120) the results are similar to those for Figs. 105 - 114. At M = 4 without addition of sodium hydroxide (Fig. 115 ; written in abbreviated form as 1 : 4 : 0), the cathode efficiency is so low that the nitric acid completely dissolves all the zinc which has been deposited. The reverse side of the panels show better coverage than that shown by the panels shown in Figs. 111 - 114.

It can be concluded therefore that as the cyanide concentration is increased, the covering power of the electrolyte improves. The matt strips are not formed so clearly as the caustic soda content is still relatively low. Gas is liberated over the whole of the panel, i.e., the cathode efficiency is markedly better than in the last series of experiments.

If the cyanide concentration is increased still further (Figs. 121 - 122) the deposit becomes leaden in appearance and may develop brown streaks. Due to the presence of the sodium hydroxide the cathode efficiency is a little better and the covering power of the bath is excellent in this region, yet the discoloured deposits are without commercial value. However, little regard is paid to the cathode efficiency in an attempt to improve the covering power of the bath ; it is useless in any event to operate the bath at M values above 4.

As shown in Fig. 123, the pure zincate electrolyte yields a coarsely crystalline deposit which, in the high current density areas, may even be spongy in character. In subsequent experiments increasing amounts of sodium cyanide were added to an electrolyte with a high caustic soda concentration. In this series of tests (212 - 214 in Fig. 104) the experiment No. 204 (Figs. 110 and 114) should fit approximately.

Increasing Cyanide Content
Figs. 118 - 120 show the back faces of Figs. 115 - 117
Front face   Back face

Fig. 115

Fig. 116

Fig. 117

Fig. 121

Fig. 118

Fig. 119

Fig. 120

Fig. 122

Front face   *For details, see Table 3, p. 71*   Front face
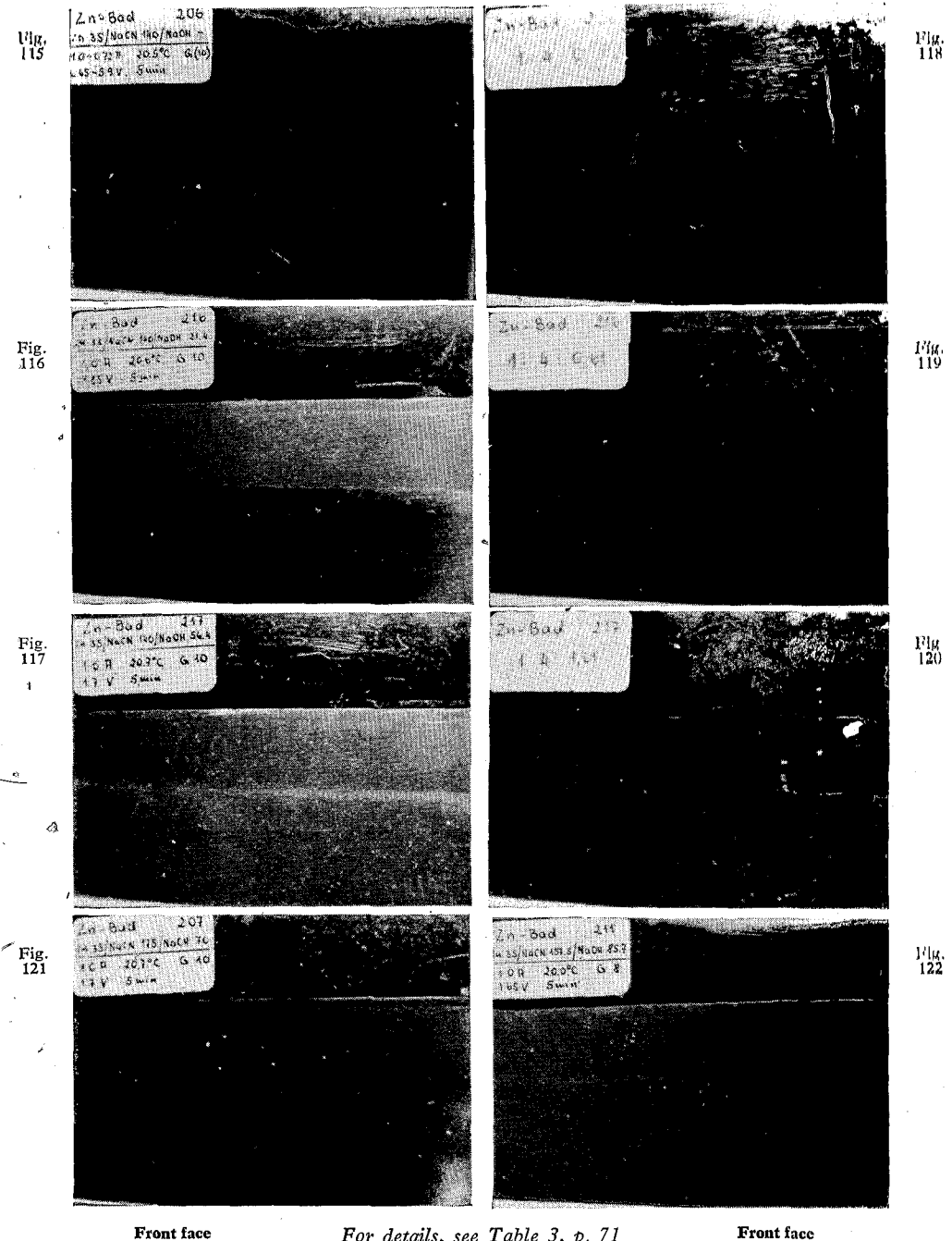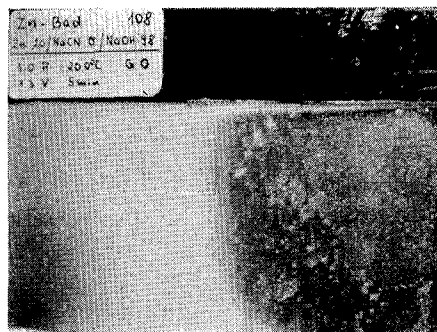
Fig. 123. Pure zincate electrolyte. See Table 3, p. 71 for details.

As is shown in Figs. 124 - 127, the matt white zinc deposit is shifted further to the low current density areas of the panel as the sodium cyanide concentration is increased. The same observations are made on the reverse sides of the panels (see Figs. 128 - 131). At the same time these panels again show that as the cyanide concentration rises, the covering power of the solution improves. The gas evolution increases and the voltage is slightly increased.

If the experiments described above have been interpreted correctly, this behaviour should be expected at lower caustic soda concentrations although in this case the region of matt deposits would not be expected to extend quite as far into the high current density range. This is confirmed in practice as seen in Figs. 132 - 135. These panels should, in fact, constitute a cross section through all the combinations of conditions shown so far and should confirm the conclusions drawn from the foregoing experiments.

Fig. 132 shows a panel plated in a zincate solution with a low cyanide content. Fig. 133 is a panel obtained in a solution in which the caustic soda concentration is only slightly higher than the sodium cyanide content. If a little more cyanide is added to this bath the object of the series of experiments would be achieved and the optimum bath composition would be determined. The cathode efficiency of the solution is good and only the covering power of the bath could be improved. In Fig. 134 the best cyanide concentration has already been slightly exceeded. The solution used for Fig. 135 is known to contain too much cyanide. The voltage varied only slightly in these four tests. Again the reverse sides of the panels show almost more than the front (Figs. 136 - 139).

Finally, it was decided to determine what kind of panel is obtained in the Hull cell using a solution in which the sum of the concentrations of caustic soda and sodium cyanide is as low as possible. Fig. 140 shows the front and Fig. 141 the reverse side of such a panel. Although in this case the solution is already in the range of an excess of cyanide, the panel shows the characteristics typical of the zincate solutions.

Increasing Cyanide Content (continued)

Front face   Back face

Fig. 124

Fig. 125

Fig. 126

Fig. 127
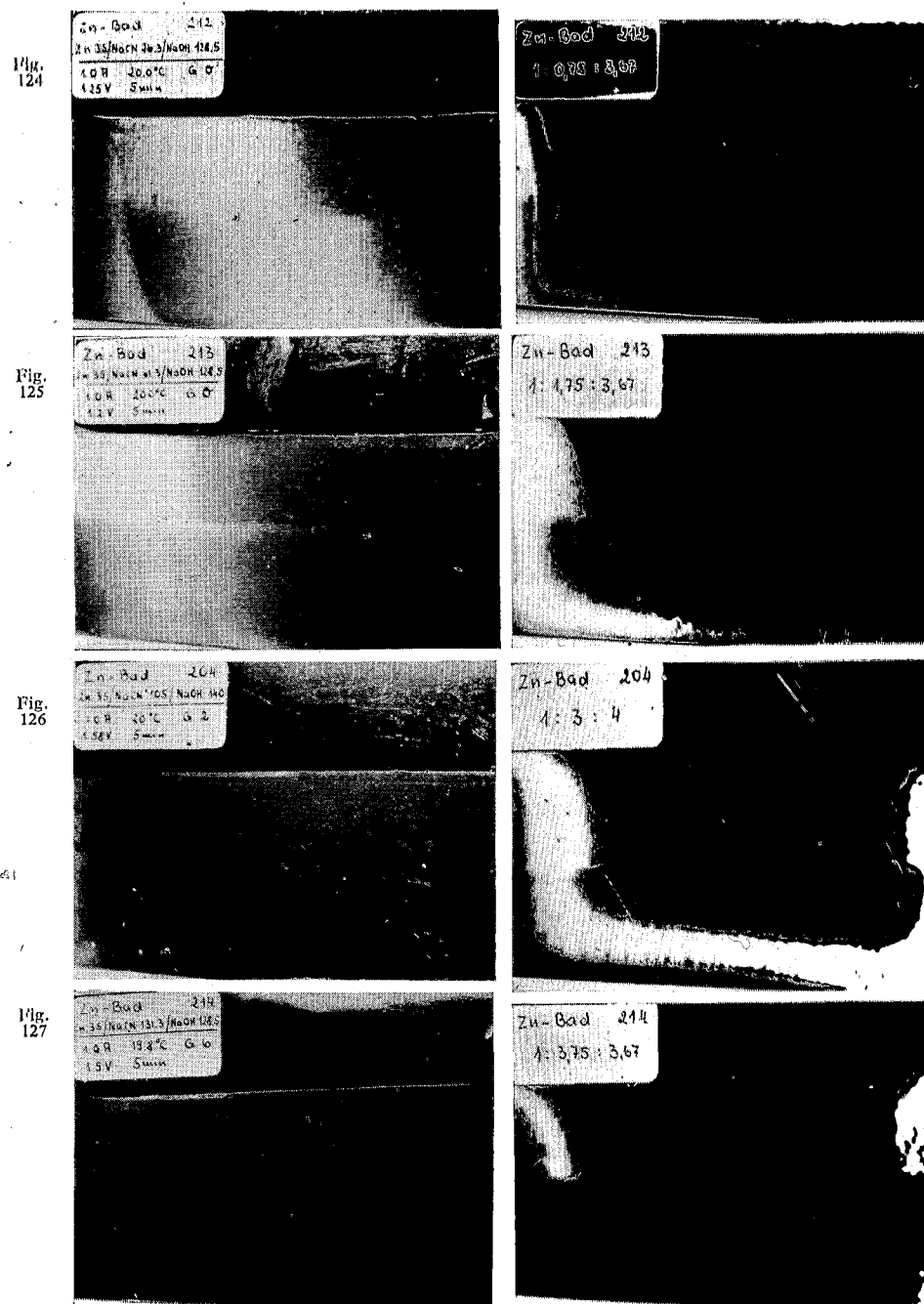
Front face   Back face

Increasing Cyanide Content (continued)

Front face   **Back face**

Fig. 132

Fig. 136

Fig. 133

Fig. 137

Fig. 134

Fig. 138

Fig. 135

Fig. 139
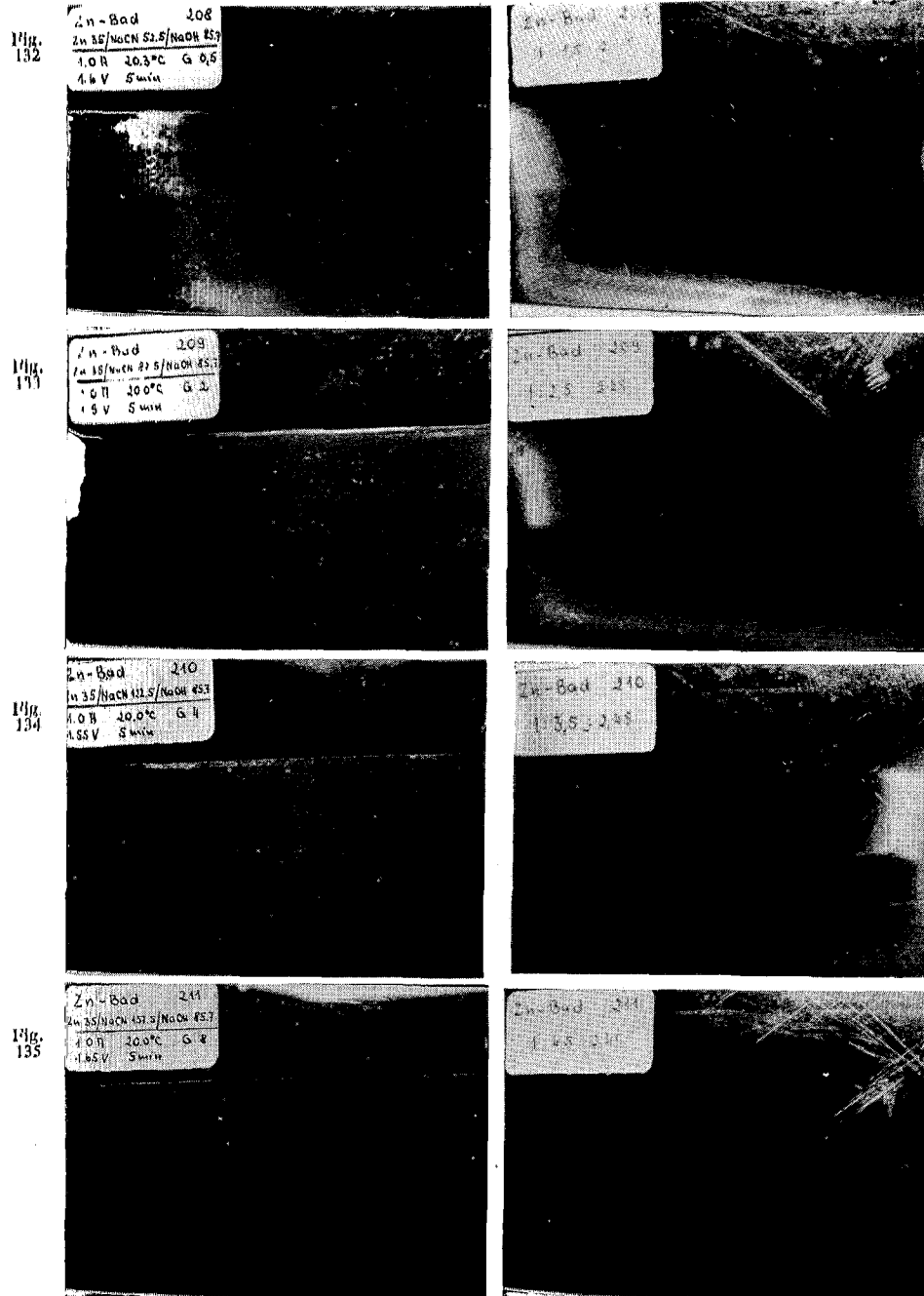
Front face   Back face

Low NaOH + NaCN

Front face   **Back face**
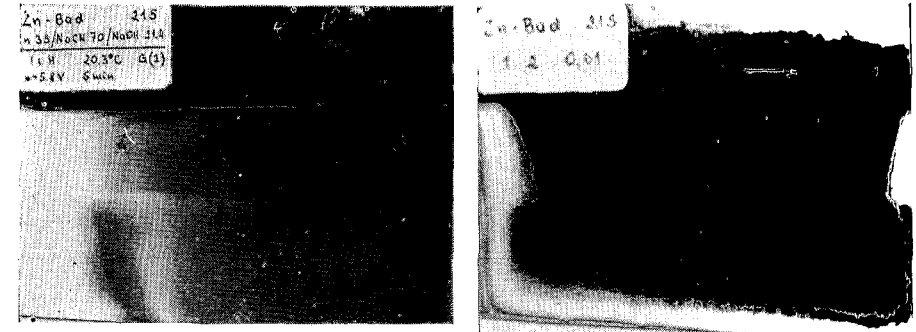
Figs. 140 (front face) and 141 (back face). When the sum of the concentrations of hydroxide and cyanide is as low as possible, the panel shows the characteristics of a zincate solution. For details, see Table 3, p. 71.

Practical implications

The following practical conclusions can be drawn from the results obtained in the experiments described in this chapter:

1. The operating range of the zinc plating solution is widened by increasing the metal concentration.
2. A solution with a composition ratio in parts by weight of Zn : NaCN : NaOH = 1 : 3 : 2.5 deposits good zinc coatings between 3 and 60 amp/sq ft at good cathode efficiency and with good covering power.
3. As the cyanide concentration increases, the covering power of the solution is improved and the cathode efficiency deteriorates.
4. The cathode efficiency improves with increase in caustic soda concentration.
5. If the composition of the solution is correct, the addition of more sodium cyanide has little effect on the conductivity. On the other hand addition of caustic soda improves the conductivity quite considerably. This is shown quite clearly in Figs. 103 and 104.

If the composition of the solution is correct the covering power is not significantly improved by raising the bath temperature. However, the higher the temperature of the solution, the further the electrolyte characteristics seem to be shifted to the zincate region. The matt areas of the deposit extend into the high current density areas (see Figs. 142 - 145). Moreover, the cathode efficiency increases as gas evolution becomes less. This behaviour must be counteracted by increasing the current density, as shown in Fig. 146.

Effect of Increasing Temperature

Fig. 142
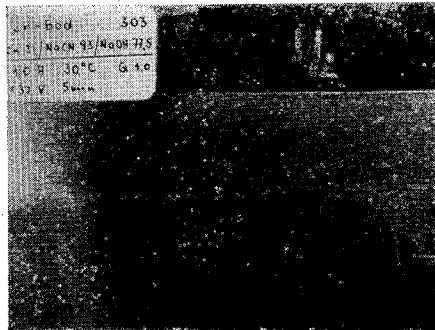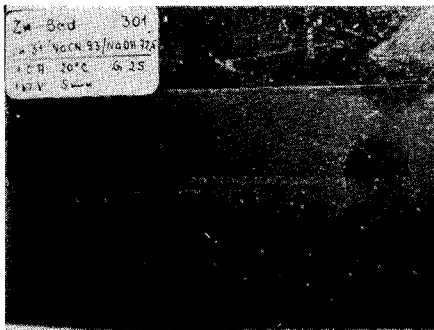
Fig. 143
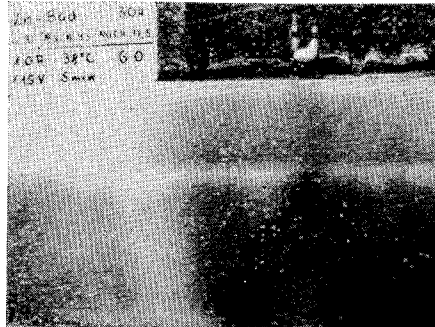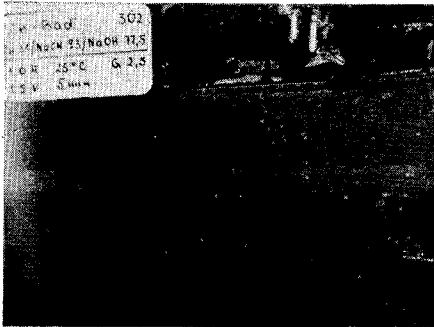
Fig. 144

Fig. 145

Figs. 142 - 145. For details, see Table 3, p. 71.

Effect of Increasing Current Density

Fig. 146. Increasing current density.
For details, see Table 3, p. 71.

By way of comparison, Fig. 146a shows Hull cell panels for three proprietary zinc plating solutions varying in their degree of brightness, all from W. Canning & Co. Ltd., Birmingham. Galvanax produces a ductile deposit which is matt and very white in appearance. Hylite is for normal bright plating while Super-Zyntax is used where maximum brightness of deposit is required.

| 80 | 50 | 30 | 20 | 12 | 6 | 2 | amp/ft² |

86 ·5·4   3·2   2·2 1·3 0·6 0·2 amp/dm²
Current 2 amperes   Time 10 minutes
Super Zyntax Bright Zinc

| 80 | 50 | 30 | 20 | 12 | 6 | 2 | amp/ft² |

8·6   5·4   3·2   2·2 1·3 0·6 0·2 amp/dm²
Current 2 amperes   Time 10 minutes
Hylite Bright Zinc

| 40 | 25 | 15 | 10 | 6 | 3 | 1 amp/ft² |

4·3   2·7   ·1·6   1·1 0·6 0·3 0·1 amp/dm²
Current 1 ampere   Time 20 minutes
Galvanax Dull Zinc
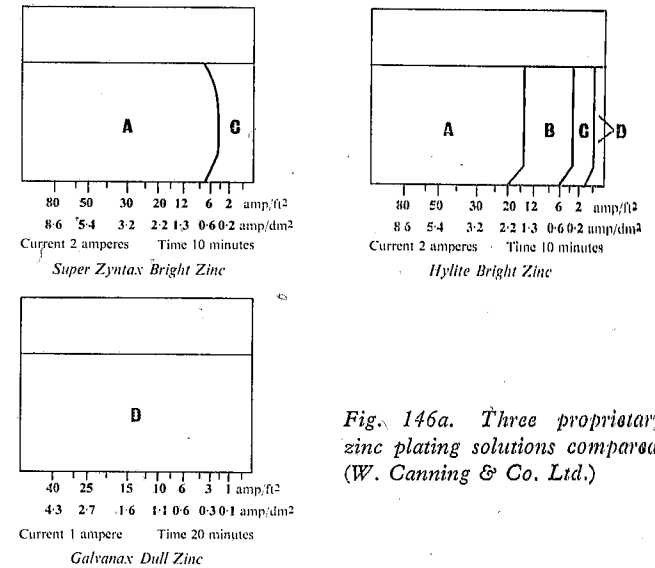
Fig. 146a. Three proprietary zinc plating solutions compared. (W. Canning & Co. Ltd.)

Effect of impurities

Copper, cadmium, silver, nickel and hexavalent chromium compounds were used in order to investigate the influence of impurities in the zinc plating bath.

While copper contamination has less effect in the cadmium cyanide bath, probably due to the higher cyanide concentration, it causes a pronounced red-brown to black coloration in the zinc bath (Fig. 147).

Hexavalent chromium prevents the formation of a coherent deposit, especially at low current densities (Fig. 148). Hence great care is required not to carry over any dichromate bright dip solution into the plating bath.

Although small concentrations of cadmium are almost completely precipitated by the sulphide in the solution, if the cadmium content is higher this is deposited preferentially on the cathode. Particularly in the high current density areas the deposit is turned yellow in colour and can no longer be brightened fully in nitric acid solution (Fig. 149).

Approximately 0·2 grams nickel added to the solution as nickel sulphate give rise to violet coloured deposits which cannot be brightened (Fig. 150).

The last two illustrations in this series show panels plated in solutions which contain silver compounds. The precipitated silver sulphide is responsible for the formation of floccular stains in the high- and medium-current density ranges. Fig. 151 shows the effect of adding a little silver plating solution, while Fig. 152 shows the effect of adding N/10 silver nitrate solution.

The influence of carbonate or brighteners on the deposit has not been investigated in the present experiments.

Effect of Impurities
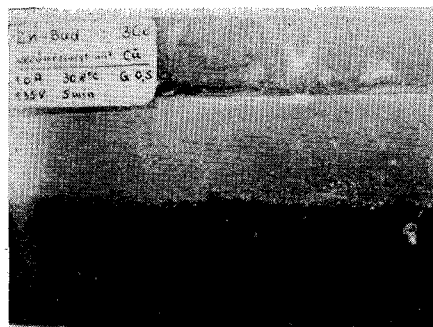
Fig. 147. Copper.
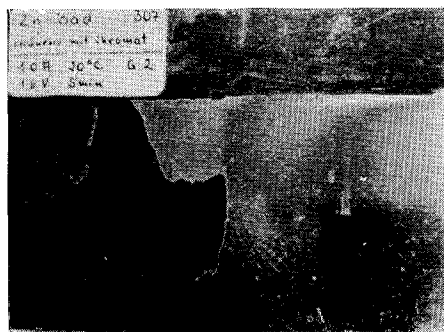
Fig. 148. Hexavalent chromium.

Effect of Impurities (continued)

Fig. 149. Cadmium.

Fig. 150. Nickel.

Fig. 151. Silver plating solution.

Fig. 152. Silver nitrate solution.

CHAPTER 8

COPPER PLATING SOLUTIONS

CONSIDERABLE DIFFICULTIES are involved in testing cyanide copper plating solutions in the Hull cell. The author has attempted many times to systematise the characteristics of Hull cell panels prepared in this solution, but except for individual cases such attempts have so far failed. The explanation for this may lie in the fact that the composition of the solution may vary within wide limits without causing significant differences in the appearance of the deposit. Nevertheless, the conclusions which can be reached from Hull cell tests on copper cyanide solutions will be discussed here.

The main constituents of the modern high-efficiency copper cyanide plating solution which are operated at elevated temperatures are copper added as copper cyanide, sodium or potassium cyanide, sodium or potassium hydroxide and, in many cases, Seignette or Rochelle salt. In order to describe the composition of the electrolytes and to obtain the specific conditions required, solutions of copper cyanide were prepared by dissolving this compound in solutions of sodium cyanide, sodium hydroxide and Seignette salt. These solutions were mixed to give the compositions required. As in the case of the cadmium and zinc plating solutions the cyanide concentrations will be presented as total cyanide in terms of the molar ratio $[(CN)] : [(Cu)]$.

1040 grams technical sodium cyanide (96% NaCN) were dissolved in approximately 3 litres water and saturated with the addition of technical copper cyanide (70·7% Cu). This was achieved partly by grinding up the lumps formed in the mixture in a mortar. Finally the solution was filtered and made up with water to a volume of 5 litres.

1040 grams technical sodium cyanide correspond to 998 grams 100% NaCN. Therefore, in accordance with equation 17:

$$CuCN + 2\,NaCN = Na_2Cu(CN)_3 \tag{17}$$

$$\frac{63\cdot57}{x} \quad \frac{98\cdot03}{998}$$

$$x = 648 \text{ g Cu}$$

if the dissolution, in fact, follows this equation and the copper present in the copper cyanide is all in the monovalent form, 648 g copper should go into solution. In one litre of the solution 129·6 g copper should be determined by analysis. The result of the determination showed the presence of 128 g copper which is considered to be in good agreement with the theoretical value.

If some divalent copper is present in the copper cyanide, as is commonly found in practice, these proportions will be altered. According to equation 18 cyanide is liberated so that only 1 mole of (CN) is required for the

$$2\,Cu(CN)_2 + H_2O = 2\,CuCN + HCN + HCNO \tag{18}$$
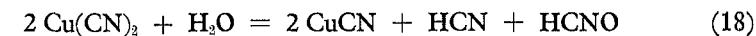
formation of the $[Cu(CN)_3]$ complex. This reaction only takes place smoothly in alkaline solution in which both the HCN and HCNO can be converted to carbonate and ammonia. If the alkalinity of the solution is insufficient the highly toxic dicyanogen $(CN)_2$ is formed:

$$2\,Cu(CN)_2 = 2\,CuCN + (CN)_2 \tag{19}$$
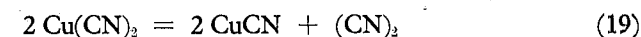
If, on the other hand, the divalent copper is present in a different compound, it will in an alkaline solution finally form copper cyanide and ammonia according to equation 20, with some loss of cyanide:

$$2\,Cu^{++} + 3\,(CN)^- + (OH)^- + H_2O = 2\,CuCN + NH_3 + CO_2 \tag{20}$$
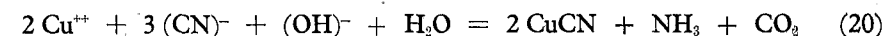
OH^- ions are always present in cyanide copper solutions, due to hydrolysis of sodium cyanide according to equation 21:

$$NaCN + H_2O \rightleftharpoons HCN + Na^+ + OH^- \tag{21}$$

In accordance with equation 18 the molar ratio $[(CN)] : [Cu]$ would not be 3 : 1 as expected but a little higher, while in the reactions given in equation 20 the molar ratio would be a little lower. The fact that these reactions take place is noted from the odour of ammonia from the solution. Moreover the present of divalent copper is clear from the slight blue coloration

which is seen when copper cyanide is dissolved in the theoretically just sufficient amount of sodium cyanide:

$$CuCN : NaCN = 1 : 1.09.$$

Although, according to the stoichiometric calculations, the sodium-copper cyanide solution contains the salt $Na_2[Cu(CN)_3]$, i.e. the molar ratio $[(CN] : [Cu] = 3 : 1$ should apply, this need not necessarily be the case. For this reason rather than describe the cyanide concentration in terms of the molar ratio, the author has preferred to describe it in terms of sodium cyanide added to the basic electrolyte composition. However, until entirely satisfactory data can be given concerning the cyanide : copper ratio in the cyanide copper plating bath, it will not be possible to carry out systematic investigations of this solution in the Hull cell. The extent of the difficulties encountered even in the attempt to determine the free cyanide concentration in the copper plating solution has been described by Nohse and Lass*, while Gabrielson has discussed the degree of complex formation of the copper in alkali cyanide solution†:

Test conditions

Cathode: brass sheet, Ms 72, polished, degreased with Vienna lime, dipped in acid ; after the test the panel was immersed in 0.5% potassium dichromate solution to prevent tarnishing.

Anode: A wire mesh anode of electrolytic copper was used to avoid excessive anode polarization and to facilitate operation at constant current density (see Fig. 164).

Current: 2 amp total current in every case. The voltage set at the beginning of the experiment fluctuated by a maximum of 0.05 volts about the nominal value.

Temperature: 63 ± 3°C.

Time of test: see Table 4.

The first step was to add increasing amounts of sodium cyanide to the basic electrolyte detailed above (Experiments 111 to 116). The appearance of the copper deposits in the high current density range was a matt light pink. In the medium current density range the copper was bright but still of the same light pink shade while at the low current density end of the panel the deposit was dark matt and finally bright and light coloured. As the

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* Galvanotechnik, 1955, No. 12.
† Metal Finishing, 1954, No. 2.

Table 4.

Solution composition (g/1 additions to the basic electrolyte) and Hull cell operating data

| Experiment no. | Fig. no | Solution, g/l additions | | | | Operating data | | | | |
		Cu	NaCN	NaOH	Seignette salt	°C	min	amps	volts	pH
111		64	0	0	0	63	5	2.0	3.75	10.5
112		64	4.93	0	0	63	5	2.0	3.7	11.0
113	133	64	9.86	0	0	63	5	2.0	3.7	11.2
114	134	64	14.79	0	0	61	5	2.0	3.8	11.2
115		64	19.72	0	0	61	5	2.0	3.8	11.3
116		64	24.65	0	0	60	5	2.0	3.65	11.5
22		64	4.93	5	0	63	5	2.0	3.5	12.5
23		64	9.86	5	0	63	5	2.0	3.2	12.5
32		64	4.93	12.5	0	62	5	2.0	3.3	13
33		64	9.86	12.5	0	63	5	2.0	3.3	
34		64	14.79	12.5	0	63	5	2.0	3.25	
35		64	19.72	12.5	0	63.5	5	2.0	3.1	
201	135	64	3.02	10.0	30	64.2	5	2.0	3.6	
202	136	64	6.08	10.0	30	63.1	5	2.0	3.55	
203	137	64	19.2	10.0	30	63.5	5	2.0	3.35	
204	138	64	23.2	10.0	30	64.5	5	2.0	3.15	
205	139	64	27.2	10.0	30	64	5	2.0	3.10	
206	140	64	30.4	10.0	30	63.5	5	2.0	3.05	

cyanide concentration was increased these ranges changed their positions on the panel, the matt light coloured region at the high current density end extending into lower current densities. At the same time the region of high gas evolution moved towards lower current densities.

The appearance of the panels changes with the angle of incidence of the light. Panels 111 to 116 which are shown in Fig. 153 differ in appearance from the same panels in Fig. 154 in which the light reached the surface at a sharp angle. In this illustration the bright parts of the surface are reproduced as light areas, in contrast to the panels shown earlier. The shift of the areas of the copper deposit of different visual appearance is clearly seen in this illustration as also is the streaking effect caused by the rising hydrogen bubbles. It is remarkable that although the sodium cyanide concentration is increasing this has little effect on the bath voltage, i.e., that in a bath of this simple composition the sodium cyanide does not act as a conducting salt.
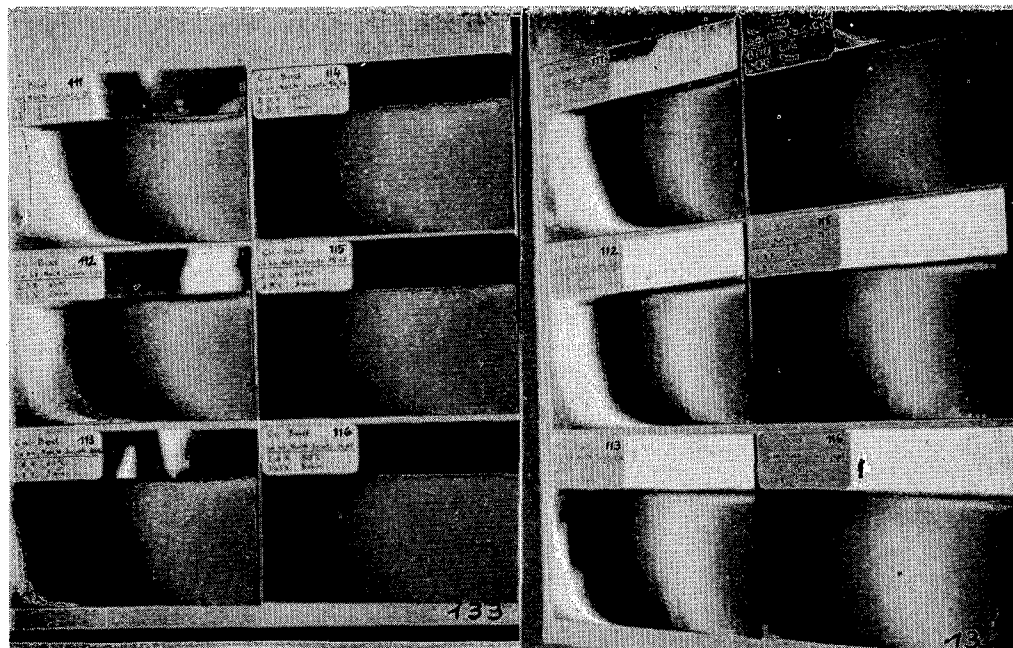
Fig. 153. Panels for experiments111 - 116 (for description see text). The composition of the electrolyte is given in Table 4, p. 87.

Fig. 154. The same panels as in experiments 111 - 116 (see Fig. 153) viewed in a strong diagonal light.

Effect of Increasing Cyanide Concentration

Figs. 155 - 160. Showing the effect of increasing cyanide concentration. For details of solution composition and Hull cell operating data, see Table 4, p. 87.

In the presence of caustic soda and Seignette salt the behaviour of the bath is quite different. In this case increasing sodium cyanide concentration reduces the voltage significantly (see Table 4). At the same time, however, the same progressive change in the appearance of the panels (see Figs. 155 to 160) is observed as in the earlier experiments (Figs. 153 and 154). Very similar panels are produced by addition of sodium hydroxide and Seignette salt, either together or singly ; these additions weaken the transition between the different regions a little.

In this connection Fig. 161 is of considerable interest. The amount of technical sodium cyanide was recalculated in terms of 100% sodium cyanide (values given on the abcissa). After thorough mixing of the solution the ' free ' cyanide content of the bath was then determined by titration (curve NaCN, titrated, 20°C). Part of the electrolyte prepared in this way was then warmed and the ' free ' cyanide concentration titrated at the operating temperature of 64°C (curve NaCN, titrated, 64°C). It is seen that the curves for the ' free ' cyanide contents at 20° and 64°C run an almost parallel course and that both

Fig. 61. Curves for 'free' cyanide concentration at 20°C and 64°C are almost parallel and, from approximately 15 g/l upwards, are practically linear.

curves, from approximately 15 g/l upwards, are practically linear, i.e. the added sodium cyanide remained as 'free' cyanide. Apparently, at this free cyanide concentration all the copper is first converted into the $[Cu(CN)_3]$ complex and it is possible that the different copper deposits on a panel may correspond to the different complexes in which the copper is present.
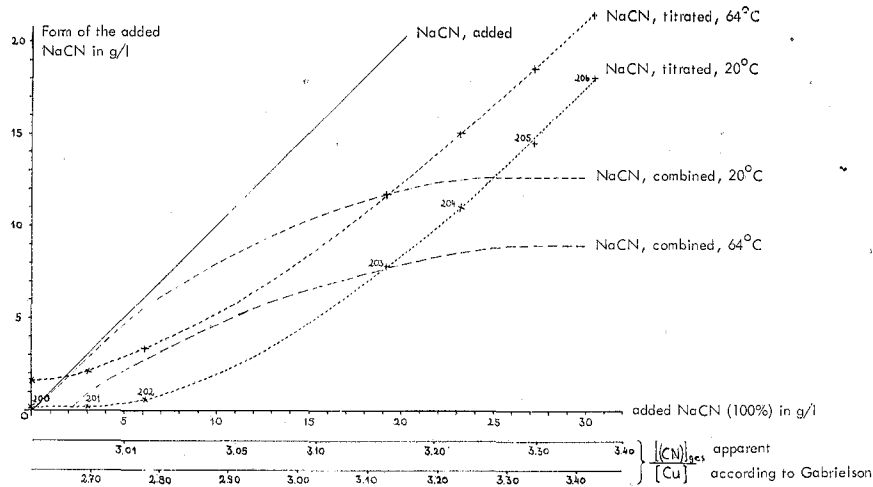
It is also noteworthy that the cold mixtures in experiments 201 to 206 (Figs. 155 to 160) are invariably blue in colour although this colour disappears when the solution is heated. If the solution is allowed to cool again, the blue colour does not return. The 'free' cyanide concentration determined by analysis is the same as before heating. Hence the disappearance of the blue colour is not connected with the consumption of any free cyanide.

Finally, in the opinion of the author, it may be concluded that it is necessary to understand the extent of the complex formation of the copper present in the plating solution at each variation in composition before it will be possible to interpret the results of Hull cell panels from the cyanide copper bath. Some further experiments carried out with copper plating solutions in the Hull cell will be described later in this book.

For comparison purposes, Fig. 161a shows Hull cell test patterns for a high efficiency fine grained matt cyanide copper plating solution (Cuprax), a bright cyanide copper (Cuprobrite) and a bright acid copper (Sulfast) while Fig. 161b shows the effect of metal contamination on a bright levelling acid copper plating solution (Cuprasol). The contamination levels given are those at which a detrimental effect on the copper deposit is first observed. These illustrations are by courtesy of W. Canning & Co. Ltd., Birmingham.
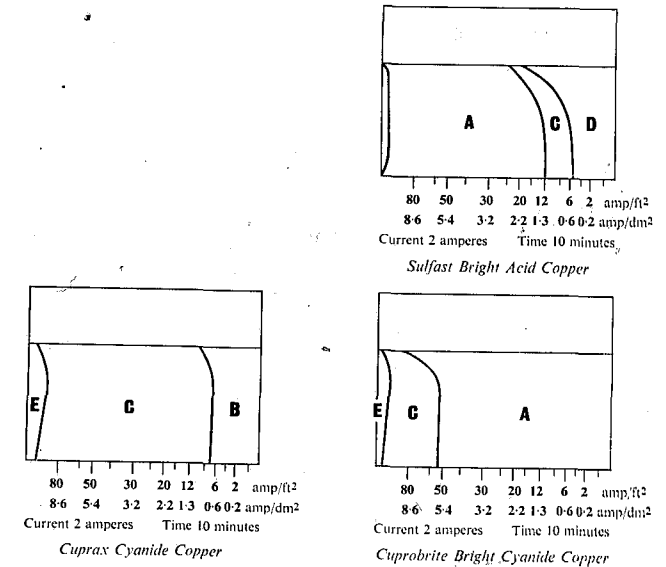

Fig. 161a. Hull cell test patterns for a high efficiency matt cyanide copper plating solution (Cuprax), a bright cyanide copper (Cuprobrite) and a bright acid copper (Sulfast). [Courtesy W. Canning & Co. Ltd.
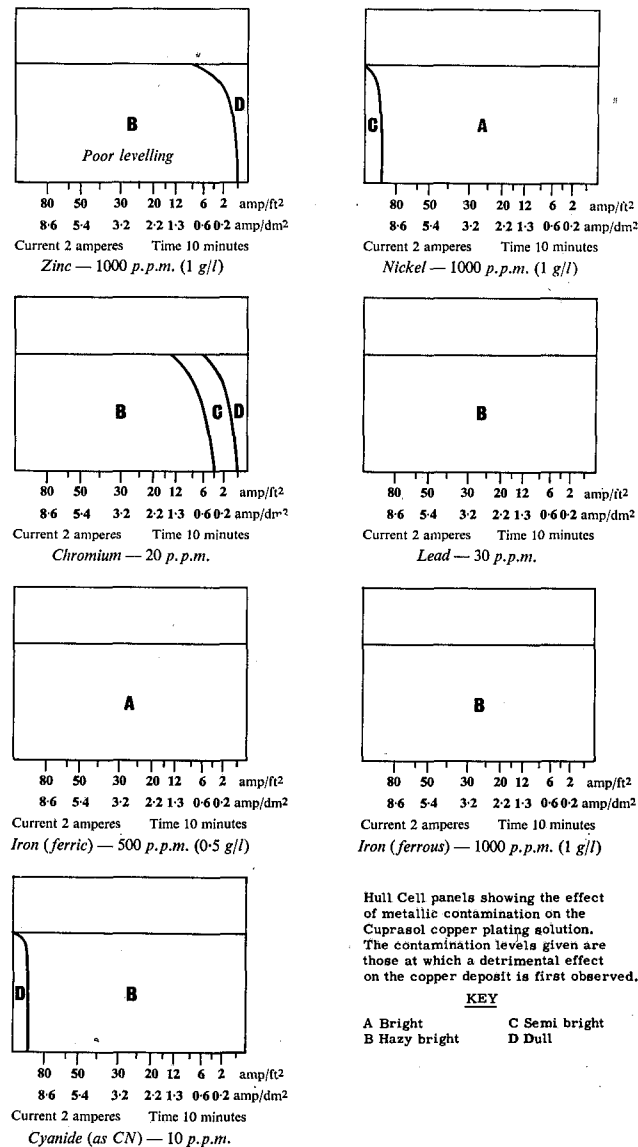
B

D

Poor levelling

| 80 | 50 | 30 | 20 12 | 6 2 | amp/ft² |
| 8·6 | 5·4 | 3·2 | 2·2 1·3 | 0·6 0·2 | amp/dm² |

Current 2 amperes   Time 10 minutes

Zinc — 1000 *p.p.m.* (1 g/l)

C   A

| 80 | 50 | 30 | 20 12 | 6 2 | amp/ft² |
| 8·6 | 5·4 | 3·2 | 2·2 1·3 | 0·6 0·2 | amp/dm² |

Current 2 amperes   Time 10 minutes

Nickel — 1000 *p.p.m.* (1 g/l)

B   C D

| 80 | 50 | 30 | 20 12 | 6 2 | amp/ft² |
| 8·6 | 5·4 | 3·2 | 2·2 1·3 | 0·6 0·2 | amp/dm² |

Current 2 amperes   Time 10 minutes

Chromium — 20 *p.p.m.*

B

| 80 | 50 | 30 | 20 12 | 6 2 | amp/ft² |
| 8·6 | 5·4 | 3·2 | 2·2 1·3 | 0·6 0·2 | amp/dm² |

Current 2 amperes   Time 10 minutes

Lead — 30 *p.p.m.*

A

| 80 | 50 | 30 | 20 12 | 6 2 | amp/ft² |
| 8·6 | 5·4 | 3·2 | 2·2 1·3 | 0·6 0·2 | amp/dm² |

Current 2 amperes   Time 10 minutes

Iron (ferric) — 500 *p.p.m.* (0·5 g/l)

B

| 80 | 50 | 30 | 20 12 | 6 2 | amp/ft² |
| 8·6 | 5·4 | 3·2 | 2·2 1·3 | 0·6 0·2 | amp/dm² |

Current 2 amperes   Time 10 minutes

Iron (ferrous) — 1000 *p.p.m.* (1 g/l)

D   B

| 80 | 50 | 30 | 20 12 | 6 2 | amp/ft² |
| 8·6 | 5·4 | 3·2 | 2·2 1·3 | 0·6 0·2 | amp/dm² |

Current 2 amperes   Time 10 minutes

Cyanide (as CN) — 10 *p.p.m.*

Hull Cell panels showing the effect
of metallic contamination on the
Cuprasol copper plating solution.
The contamination levels given are
those at which a detrimental effect
on the copper deposit is first observed.

KEY

A Bright   C Semi bright
B Hazy bright   D Dull

Fig. 161b. Showing the effect of metal contamination on a bright acid copper plating solution (Cuprasol ; W. Canning & Co. Ltd.). The contamination levels given are those at which a detrimental effect on the copper deposit is first observed.

CHAPTER 9

BRASS, TIN, SILVER AND MISCELLANEOUS PLATING SOLUTIONS

(Contributed by R. O. Hull & Company Inc., Cleveland, Ohio)

Brass plating baths

H U L L C E L L plating tests of brass plating baths provide a very interesting method for learning the fundamental principles underlying the operation of this complex plating system. Some of the reasons for the unusual, but predictable, behaviour of brass are as follows:

1. Zinc is plated from the bivalent state while copper is from the mono-valent state.
2. Zinc can exist as complexes of sodium-zinc cyanide or sodium zincate (both present in brass), whereas copper can exist in the form of one or more complexes only with sodium cyanide, dependent upon temperature.
3. Changes in pH change the ratio of copper to zinc deposited, but two ranges are usable.

In the Hull cell test, a steel plate cathode is used at a total current of one ampere for 5 to 10 minutes. A brass or steel anode may be used. The temperature of the plating bath should be that intended for practical operation, which is usually about 95°F. A satisfactory composition of bath gives a bright yellow or greenish yellow plate from 1 to 40 amp/sq ft on the Hull cell plate.

The simplest method of bath control in the absence of chemical analysis and pH measurement is observation of the colour of the brass deposit. If the brass deposit is of the desired yellow or yellow-green colour, the composition is approximately 70% to 80% copper, the balance being zinc. A pink or reddish colour results from either too high or too low a proportion of zinc in the deposit.

The first point to determine in correcting a brass bath is whether the zinc content of the deposit is too high or too low. The procedure for this is as follows:

1. Make a plate noting the colour and plating range. If the colour is good but the width of plating range is narrow, the proportion of constituents is about right. The range can usually be widened by addition of both heavy metal cyanides with sodium cyanide.

2. If the plate is not a uniform yellow or yellow-green colour, take two portions of the bath, add one ounce per gallon sodium bicarbonate to one portion and 0·5 ounce per gallon caustic soda to the other. In the first case, the pH is lowered and hence the zinc content of deposit is decreased. The reverse is true of the second portion. This procedure should be repeated on the same portions but with double the respective additions, noting which addition improves the deposit colour (high zinc in the deposit produces a characteristic orange-brown powdery deposit at low current densities).

If the bicarbonate addition improves the deposit, the bath can be corrected by any of the following additions to increase the ratio of copper to zinc in the deposit:

1. Adding bicarbonate to lower the pH, or
2. Adding copper cyanide, or
3. Adding sodium cyanide to raise the free cyanide content.

If the caustic soda addition improves the deposit, the bath can be corrected by any of the following additions to decrease the ratio of copper to zinc in the deposit:

1. Adding caustic soda to raise pH, or
2. Adding zinc cyanide, or
3. Adding both copper cyanide and zinc cyanide to decrease the free cyanide content.

The zinc content of the deposit can be reduced by (1) decreasing zinc cyanide in the bath ; (2) lowering the pH of the bath ; (3) increasing free cyanide of the bath ; and to a lesser degree (4) raising the temperature ; (5) raising the cathode current density ; or (6) increasing thickness of deposit (up to about 0.00013 inch). The reverse of these increases the zinc content of the deposit.

The addition of either copper cyanide or zinc cyanide tends to lower the bath pH, whereas sodium cyanide addition tends to raise the bath pH and consequently the pH should be measured and controlled. The best pH value

depends chiefly upon the metal cyanide ratio in the bath. For control purposes the following table may be used as a guide.

Ratio $CuCN : Zn(CN)_2$	Optimum pH (electrometric)
3 : 2 (rubber adhesion)	10·3 (range 10·1 – 10·5)
3 : 1	12 (range 11.5 – 12.5)

The pH range of 10·5 to 11·5 is not normally used because of the tendency toward streaky, irregular deposits.

Ammonium hydroxide nearly always improves colour of deposit, unless the bath composition and pH are almost ideal. Sodium carbonate should be present, and new baths should have 5 oz/gal included in the formulation.

In general, the above procedure will restore almost any brass bath to operation even without chemical analysis, since acceptable deposits are obtainable over a wide range of bath compositions. It is very important, however, that only one component be varied in any one plating test, since the multiple functions of some of the ingredients frequently tend to confuse the apparent trend. Thus, adding sodium cyanide tends to raise the pH, which should promote zinc deposition, but this effect is more than counteracted by the decreased cathode efficiency with respect to zinc, so that usually a lower percentage zinc is deposited.

Impurities are encountered only infrequently. Lead tends to make a dark, dull deposit. Arsenic (sometimes suggested as a brightener) tends to produce white deposits.

Only experience in making such tests will make clear the terms "white", "pink", etc., applied to the commercial deposits, but by following the above plan of brass plating solution diagnosis it is possible to match any required colour of deposit.

Alkaline tin baths

The alkaline stannate tin bath lends itself quite well to control by plating tests. It must be operated with considerable care to avoid certain conditions which, however, are usually corrected without much difficulty.

For plating tests a steel cathode is used with a total current of 2 amperes for 5 to 10 minutes at 175°F and a tin anode. It is desirable to heat the tin plating bath to about 190°F before putting it in the Hull cell. The solution sample should be light yellow or straw coloured. If it is very dark in colour, stannous ions are probably present and should be oxidised with a small amount of hydrogen peroxide.

Optimum composition: smooth white deposits are produced at from 2 to 50 amp/sq ft. Moderate variations in sodium stannate content are not perceptible on the Hull cell cathode.

High caustic soda: spongy deposits.

Low caustic soda content: poor conductivity ; anodes do not acquire a yellow film.

Stannous tin: dark, rough deposits.

Low tin content: very low cathode efficiency.

High tin content: No noticeable effect on the cathode.

Sodium acetate high or low: little effect on cathode, except possibly slightly smoother cathode with acetate.

Cyanide silver baths

Hull cell tests provide a rapid means for checking cyanide silver baths with respect to overall composition and brightening agents. A silver anode should be used which may be cut to size out of ordinary sheet silver. A total current of one ampere should be used for conventional silver plating baths for 10 minutes.

Normal concentration (AgCN 4 oz/gal, pH 11·5): Smooth deposits at 2 to 6 amps/sq ft, burnt above 10 amp/sq ft.

Normal concentration plus agitation: Semi-bright at 1 to 10 amp/sq ft, smooth to 35 amp/sq ft.

Low overall concentration: smooth deposits at 1 to 2 amp/sq ft, burnt above 5 amp/sq ft.

High overall concentration: semi-bright at 1 to 10 amp/sq ft, smooth to 40 amp/sq ft.

Low free cyanide: dull deposits, poor adherence.

High free cyanide: improved covering, decreased cathode efficiency.

Low carbonate: no effect noticed on cathode ; decreased conductivity ; anode polarization.

High carbonate (over 12 oz/gal K_2CO_3): deposits somewhat dull.

Low pH (about 10): low bright range, smooth deposits at 1 to 3 amp/sq ft.

High pH (about 13): rough, burnt deposits over entire plate.

Brightener: check with supplier of proprietary process.

Miscellaneous plating baths

Numerous other plating processes lend themselves to Hull cell test control, and the effect of each variable in each process gives definite information on simplified control. Such processes as lead, black nickel, gold, platinum, indium and alloy plating systems are examples of its applicability. Information on details of Hull cell tests may be obtained from the originators of such processes or determined by the operator for the particular needs of each process or operation.

CHAPTER 10

TESTING OF NICKEL SALTS

*by Ing.-Chem. Walter Nohse and Ing. G. Wagenblast**

THIS CHAPTER describes experiments in which nickel plating salts have been compared by the appearance of the deposits on Hull cell test panels. The chemical analysis of these salts is shown in Tables 5 - 8.

For the Hull cell tests, 100 g of the salts were dissolved in deionised water and made up to 1000 ml in a measuring flask. Solid impurities were allowed to settle out and the solution filtered through filter paper. 250 ml of the filtrate were transferred to the Hull cell and the test carried out under the following conditions using a polished and degreased brass sheet cathode:

temperature of solution	50°C
current density	0·25 amp/panel
time	10 minutes
voltage	adjustable
pH of solution	varied with additions.

The anode should be a high-efficiency plating anode activated in a nickel stripping solution. The high current density range is situated on the left hand side of the panel.

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* Reprinted from *Galvanotechnik*, 1963, 54, No. 6, 331 - 5.

Table 5. Chemical analysis of laboratory reagent grade nickel chloride

Metal ions (%)		Salt content (%)		Max impurities (%)
Ni^{++}	25.0	30.0	Cl^-	
Fe^{++}	0.0017	0.0063	$FeCl_2.4H_2O$	0.005
Cu^{++}	0.0007	0.0015	$CuCl_2$	0.005
Pb^{++}	0.0002	0.0003	$PbCl_2$	0.001
Zn^{++}	0.0006	0.0015	$ZnCl_2.1\frac{1}{2}H_2O$	0.005

Table 6. Chemical analysis of electroplating quality nickel chloride

Metal ions (%)		Salt content (%)		Max impurities (%) Hc 50970	Nc 50970
Ni^{++}	24.5	29.1	Cl^-		
Fe^{++}	0.0031	0.0110	$FeCl_2.4H_2O$	0.010	0.05
Cu^{++}	0.0008	0.0017	$CuCl_2$	0.002	0.01
Pb^{++}	0.0005	0.0007	$PbCl_2$	0.002	0.01
Zn^{++}	0.0120	0.0300	$ZnCl_2.1\frac{1}{2}H_2O$	0.010	0.01

Table 7. Chemical analysis of laboratory reagent grade nickel sulphate

Metal ions (%)		Salt content (%)		Max impurities (%)
Ni^{++}	20.85			
Fe^{++}	0.0008	0.0049	$FeSO_4.7H_2O$	0.001
Cu^{++}	0.0010	0.0039	$CuSO_4.5H_2O$	0.005
Pb^{++}	0.0001	0.0002	$PbSO_4$	0.001
Zn^{++}	0.0110	0.0440	$ZnSO_4.7H_2O$	0.050

Table 8. Chemical analysis of electroplating quality nickel sulphate

Metal ions (%)		Salt content (%)		Max impurities (%) Hs 50970	Ns 50970
Ni^{++}	22.1				
Fe^{++}	0.0014	0.0069	$FeSO_4.7H_2O$	0.005	0.03
Cu^{++}	0.0035	0.0136	$CuSO_4.5H_2O$	0.002	0.01
Pb^{++}	0.0005	0.0007	$PbSO_4$	0.002	0.02
Zn^{++}	0.0080	0.0352	$ZnSO_4.7H_2O$	0.010	0.01

Nickel chloride

The basic electrolyte made up from the reagent grade nickel chloride had a pH value of 3·9 ; that made up from the electroplating quality material had a pH of 5·8 and a sediment could be seen. The pH was adjusted to pH 3·9 with the aid of pH papers and both solutions were electrolysed at the same total current.

Figs. 162 and 163 show the deposits obtained by the two solutions and confirm a substantial difference between the two salts. Noteworthy features are the failure to deposit nickel in the second half of the panel in Fig. 163, i.e. in the electroplating quality nickel chloride ; the high current density end of the panel the nickel deposit is mixed with deposits of nickel salt as $Ni(OH)_2$. On the other hand, the panel shown in Fig. 162 is covered with nickel completely, although metallic impurities are codeposited in the current density range around 5 amp/sq ft ; elsewhere the coating remains matt or dark and slightly reflective.

The pH of further 250 ml samples was then adjusted to pH 5·8 with 10 per cent sodium hydroxide solution and electrolysis repeated. The nickel deposit plated from the reagent grade solution under these conditions is seen in Fig. 164 while Fig. 165 shows the coating obtained from the nickel chloride of electroplating quality. In the latter the metallic impurities are seen to be deposited in the centre ; at lower current densities the nickel deposit is bright.

If Fig. 162 is compared with Fig. 164 it can be seen that the latter shows brighter and heavier deposits at the low current density side of the panel, and demonstrates that the purer nickel salt deposits better nickel coatings.

Next, iron, copper, lead and zinc were added to the solution in the concentrations noted in Table 9 and the solutions were electrolysed at pH 5·8.

Table 9. Additions of metallic impurities to nickel chloride solution

Impurity	Concentration (%)	Salt content (g)	Addition per 100 g salt
Fe^{++}	0.05	0.1780 - 0.0063	0.1717 g $FeCl_2.4H_2O$
Cu^{++}	0.01	0.0210 - 0.0015	0.0195 g $CuCl_2$
Pb^{++}	0.02	0.0270 - 0.0003	0.0267 g $PbCl_2$
Zn^{++}	0.05	0.1250 - 0.0015	0.1235 g $ZnCl.1\frac{1}{2}H_2O$

In some cases the iron was precipitated from the solution as ferric hydroxide. Fig. 166 shows the deposit which was obtained and which, over a part of the panel, was in a semi-bright form. At higher current densities a dark streak was obtained whereas only a thin nickel deposit was plated at low current densities.

Fig. 162. Reagent-grade nickel chloride, pH 3.9.
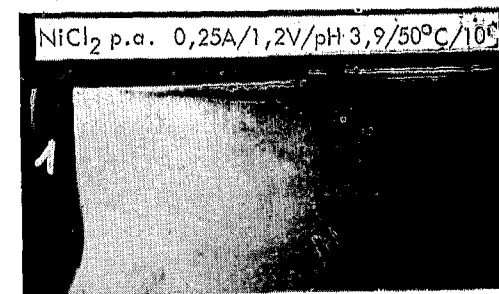
Fig. 163. Electroplating-grade nickel chloride, pH 3·9.
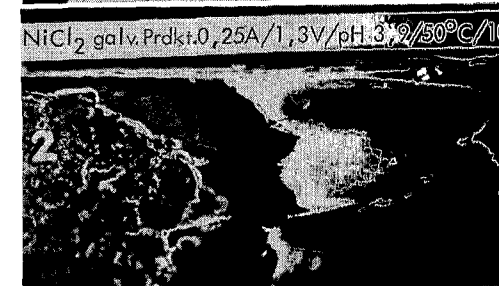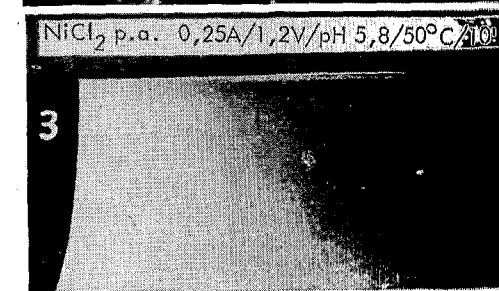
Fig. 164. Reagent-grade nickel chloride, pH 5·8.

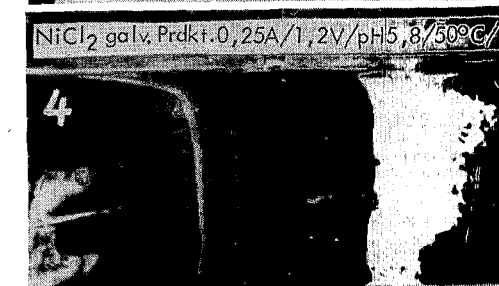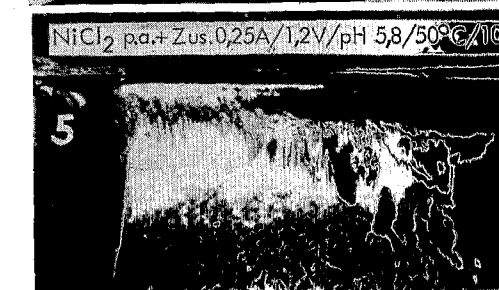Fig. 165. Electroplating-grade nickel chloride, pH 5·8.

Fig. 166. Precipitation of iron as ferric hydroxide.

Nickel sulphate

Samples of laboratory reagent grade and electroplating grade nickel sulphate were tested in the same manner as the nickel chloride. The pH of the reagent grade nickel sulphate solution was 3·6 while that of the electroplating quality salt was 5·5. The latter solution was adjusted to pH 3·6 with 1 : 1 sulphuric acid solution and both solutions were then electrolysed.

The coatings obtained on the panels are seen in Figs. 167 and 168. The electrolyte prepared from the reagent grade nickel sulphate gave a bright nickel deposit and, mainly in the high current density area, the coating was flecked with black streaks. In Fig. 168 (electroplating grade) these streaks were rather more pronounced and the deposit showed small dark pores.

In further experiments carried out at pH 5·5 (adjusted with 10 per cent caustic soda solution), pure nickel sulphate solution plated a bright nickel deposit over practically the whole current density range and only in small areas did matt patches appear on the surface (see Fig. 169). No metallic impurities appeared to be deposited on the panel. In the panel illustrated in Fig. 170, on the other hand, in which the bath was made up with the electroplating quality nickel sulphate, metallic impurities were codeposited with the nickel. As in the earlier experiment it can be shown that the purer grade of nickel sulphate yields a better nickel deposit and that this is most apparent in high pH solutions.

Fig. 171 shows a deposit from a reagent grade nickel sulphate solution which contains the maximum permissible impurity concentrations of iron, copper, lead and zinc quoted in German Standard Specification DIN 50 970, Nickel Salts for Nickel Plating Baths (see Table 10). In this case too, ferric

Table 10. Additions of metallic impurities to nickel sulphate solution

Impurity	Concentration (%)	Salt content (g)	Addition per 100 g salt
Fe^{++}	0.005	0.0250 - 0.0049	0.0196 g $FeSO_4.7H_2O$
Cu^{++}	0.002	0.0078 - 0.0039	0.0039 g $CuSO_4.5H_2O$
Pb^{++}	·0.002	0.0029	0.0029 g $PbSO_4$
Zn^{++}	0.010	0.0440 - 0.0440	0 g $ZnSO_4.7H_2O$

hydroxide was precipitated when the solution was electrolysed at pH 5·5. At the high current density end of the panel the metallic impurities were plated out in the form of a wide, black streak and several narrower streaks. The remainder of the coating was semi-bright and did not cover the basis metal surface completely in the low current density range.

From Figs. 170 and 171 it can be concluded that the nickel deposit is affected by increasing contamination of the salts.

Fig. 167. Reagent-grade nickel sulphate, pH 3·6.
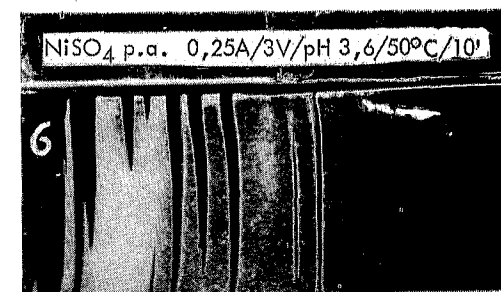
Fig. 168. Electroplating-grade nickel sulphate, pH 3·6.

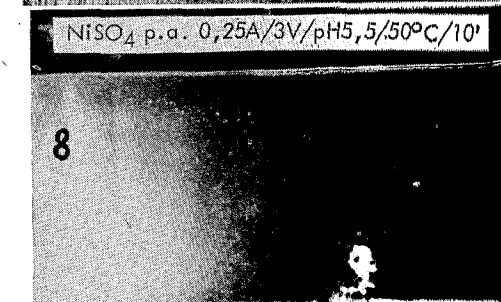Fig. 169. Reagent-grade nickel sulphate, pH 5·5.

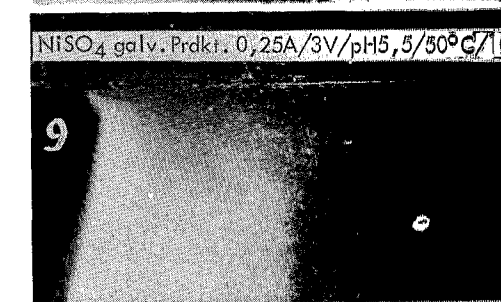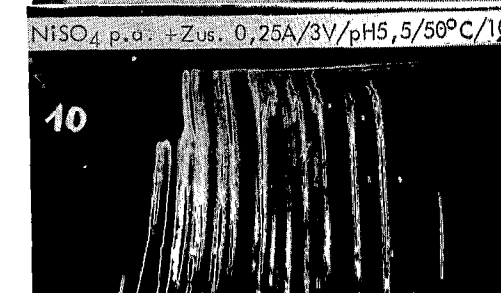Fig. 170. Electroplating-grade nickel sulphate, pH 5·5.

Fig. 171. Reagent-grade nickel sulphate plus impurities detailed in Table 10 (opposite), showing precipitation of ferric hydroxide when electrolysed at pH 5·5.
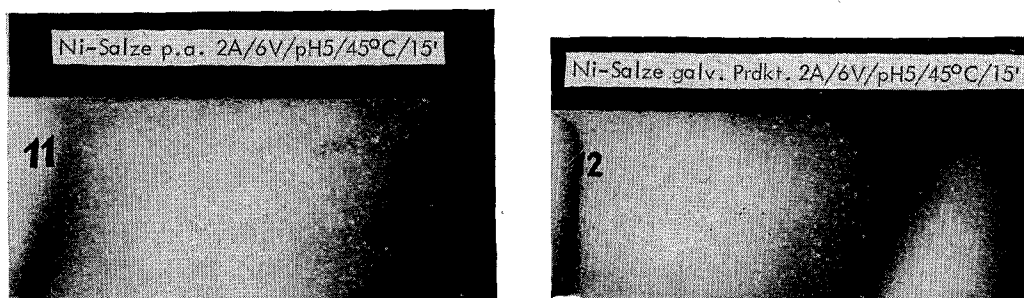
Nickel plating salts

As a final experiment in this series, solutions were made up containing:

nickel sulphate (both grades)   240 g/l
nickel chloride (both grades)   45 g/l
boric acid   30 g/l

and Hull cell tests were run at:

current density   2 amp per panel
temperature   45°C
plating time   15 minutes
voltage   adjustable
pH   5·0

The panels obtained, which are shown in Figs. 172 and 173 respectively, hardly differ in their appearance. In the low current density range bright deposits were plated in both cases. The electroplating grade solution showed pits at high current densities (Fig. 173) but in all other respects the coatings from both baths complied with specification requirements.

Figs. 172 and 173. Nickel plating solutions made up from reagent grade (left) and technical grade (right) salts.

Conclusion

The metallic impurities present in the nickel salts are, for the most part, deposited at about 5 amp/sq ft. The Hull cell is a useful method for testing the quality of plating solutions made up from different grades of nickel salts as well as for measuring the covering power of the solutions. By varying the pH, it is possible to achieve considerable differences in the behaviour of the solutions.

CHAPTER 11

METAL AND CURRENT DISTRIBUTION

Part 1. Use of the Jet Test Plus Hull Cell to Determine Metal Distribution

THE JET method of local thickness testing can be used to examine the metal distribution of electrodeposits on Hull cell panels. Thus, Fig. 174 shows the metal distribution determined in this way on a Hull cell panel plated at 2·0 amp in a bright nickel plating solution with low brightener concentration. Fig. 175 shows the same type of test in a well balanced bright nickel bath while Fig. 176 shows a test carried out on a copper plating bath.

Fig. 177 shows the results for the metal distribution obtained in experiments 201, 205 and 206 with a cyanide copper plating solution (see Table 4, p. 87). The curves of experiments 202, 203 and 204 lie between those for experiments 201 and 205. It is clearly seen that as the cyanide content of the solution is increased the cathode efficiency is reduced.

If, instead of the penetration time, it is required to measure the actual local deposit thickness at the points referred to and thus to determine the cathode efficiency quantitatively, the test solution must be standardised. If the current densities are plotted linearly, instead of in the regular logarithmic curve, the course of the metal distribution curve is somewhat different (see Fig. 178). If the deposition process took place entirely without polarization, the result would be a diagonal straight line. The higher the cathode polarization, the more the metal distribution curve deviates from the linear. In this case it is seen that the cathode polarization in the cyanide copper plating bath increases with increasing cyanide concentration, particularly in the range between 90 and 140 amp/sq ft.

Metal Distribution

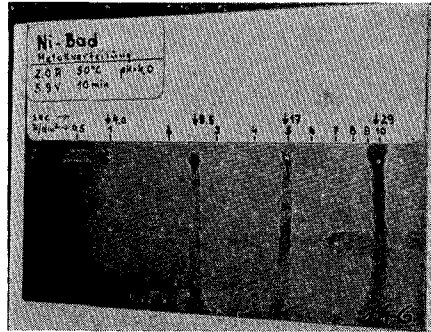Fig. 174. Bright nickel plating solution with low brightener concentration.

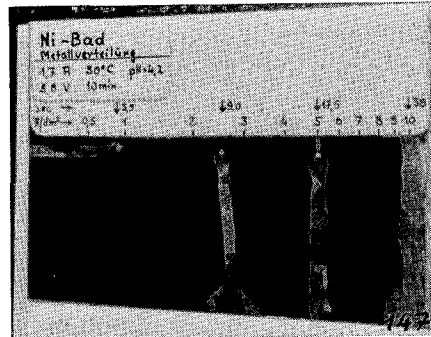Fig. 175. Well-balanced bright nickel plating bath.
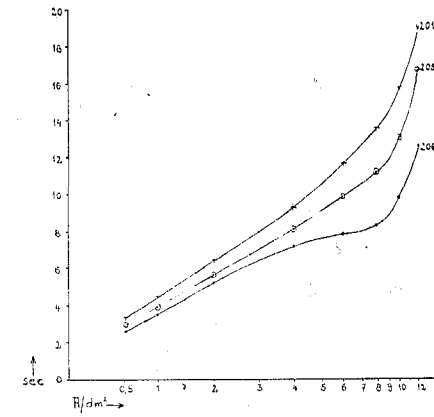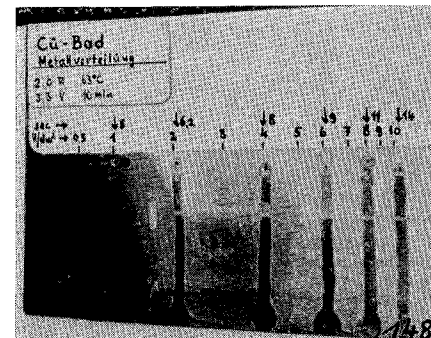

Fig. 176. Copper plating bath.

Fig. 177. Warm copper plating in the Hull cell. Coating thickness distribution on the panel, measured by means of an empirical test solution, as a function of cyanide concentration (cell current—2 amp).
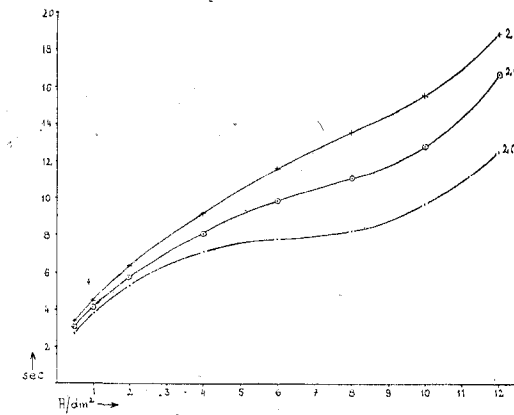

Fig. 178. Warm copper plating in the Hull cell. Local penetration time as a function of current density and cyanide concentration (cell current—2 amp).

Fig. 179 and 180 compare the metal distribution on Hull cell panels plated in an acid copper bath and a bright nickel solution. Neither of these panels shows any significant degree of cathode polarization. Compared with the results of panels plated in the cyanide copper bath it is clearly shown that the latter plates thicker deposits in the low current density areas than the acid copper bath but the reverse is true at high current densities. These results naturally assume that the rate of dissolution in the test solution of the copper deposits from the acid and cyanide baths is similar. The actual times for penetration to occur do not permit a comparison of the actual coating thicknesses between the copper and nickel solutions as (i) the values were divided by a factor of 2 for convenience and (ii) the test solution employed takes considerably longer to penetrate a nickel deposit than a copper coating of the same thickness. Although, therefore, the slopes of the curves in Figs. 179 and 180 are similar, it is important not to draw wrong conclusions from this.
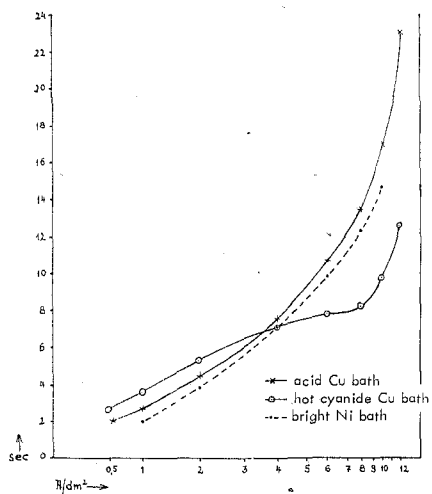
Fig. 179. Metal distribution on Hull cell panels : natural logarithmic current density curve.
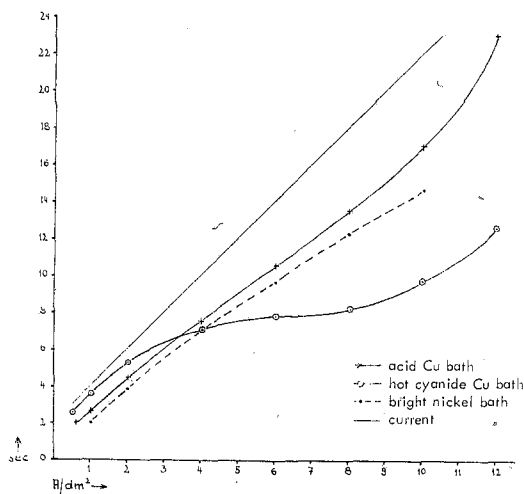
Fig. 180. Metal distribution on Hull cell panels : linear current density curve.

Part 2. Direct determination of current and metal distribution

by Dr. Josef Heyes

Two previous workers, Rousselot and Watson, have used the Hull cell for investigating the throwing power of electroplating solutions. The first named determined the extent to which the commencement of chromium deposition on a Hull cell panel depended on the current density, temperature, sulphuric acid concentration and other variables. For this purpose he employed divided electrodes. In order to measure the current distribution over the panel he changed the potential of one part of the cathode to the value reached by the other part of the cathode and noted the electrical resistance which was required to be inserted into the circuit to achieve this. From this and a knowledge of the electrode area, current density at both parts of the electrodes could then be calculated.

In England Watson deposited metal coatings on Hull cell panels plated in different plating solutions, sectioned the panels and determined the coating thicknesses at different points with the aid of a metallurgical microscope. His method required the preparation of several metallographic sections.

Before concerning ourselves with the determination of the metal distribution, we ourselves attempted to investigate current distribution by means of divided electrodes, but failed to achieve any useful results.

Similar investigations of current distribution were carried out in the 1930's by Mantzell. These investigations suffered the disadvantage, however, that an ammeter was inserted into the circuits of the part-electrodes in series. The changes caused by this method in the electrical resistance of the various individual circuits led to poor results, nor was the method improved significantly by considering the instrument resistances in the calculation. The primary current distribution in the Hull cell depends predominantly on the latter's geometrical shape, which is responsible for the electrical field strength at each point of the cell. The local current density is, however, a function of the secondary current distribution which in turn depends on the so-called polarization. Polarization is the result of inhibition of the transfer of metal ions from the solution into the crystal lattice of the metal, and also of the impoverishment of the liquid film at the metal-solution interface with respect to metal ions. To all intents and purposes, therefore, polarization is an additional electrical resistance in the circuit situated at the metal surface.

To measure the current distribution we employed the circuit shown in Fig. 181 which avoids the difficulties encountered in the circuits described by Rousselot and Watson. The Hull cell electrode is divided into 7 parts. A resistance of 0.1 ohm is placed behind each electrode. This resistance is quite small in comparison with that of the electrolyte. If a voltmeter is connected
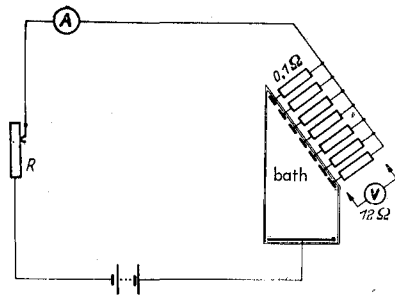
Fig. 181. Circuit diagram of a Hull cell with divided anode or cathode.

in parallel to the 0·1 ohm resistance and if the external resistance of the voltmeter is appreciably higher than 0·1 ohm, the current which flows through the whole of the circuit is virtually unaffected. In this way it is possible to obtain a reliable value for the partial current by determining the voltage drop at the resistances behind each of the electrodes. The total current flowing through the whole of the circuit is measured by the galvanometer A. Some of the results obtained by these experiments are given below.

Fig. 182 shows the current distribution of an acid copper perchlorate electrolyte with and without the addition of a brightener, at a total current of 0·2 amp. The copper concentration of the solution was 130 g/l and the perchloric acid content was 30 g/l. It is clear that the addition of the brightener improves the current distribution in the Hull cell. The probability is that the current distribution is predominantly a function of the increase in polariza-
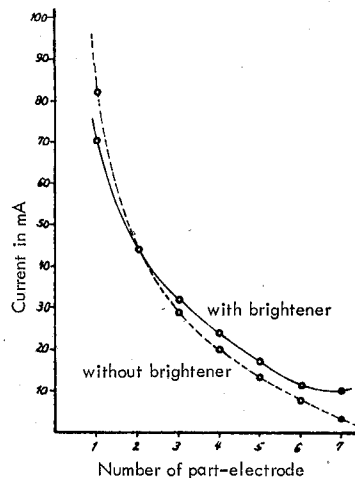
Fig. 182. Current distribution in an acid copper perchlorate electrolyte.
copper concentration   130 g/l
current   0.2 amp
perchloric acid concentration
   30 g/l
brightener   4 ml W/l + 12·3 ml V/l
—— with brightener
– – – – without brightener

tion due to the presence of the brightener. The results comprise the mean of two series. It is noteworthy that the sum of the part-currents agrees very well with the total current.

The second series of experiments was designed to determine the influence of the acid concentration of the solution on current distribution. If the total current is maintained constant there is little effect by the acid content on the current distribution in the solution investigated (see Fig. 183).
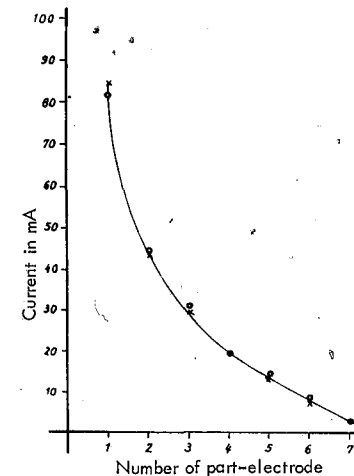
Fig. 183. Effect of perchloric acid concentration on current distribution.
copper concentration   130 g/l
current   0·2 amp
perchloric acid concentration:
   x   50 g/l
   o   30 g/l

Fig. 184 shows that the same method may also be applied to the study of anodic processes. In this graph the current distribution on a steel surface has been determined during electropolishing in an acetic acid-perchloric acid solution. In this case a smaller electrode area was used in the experiments principally because the applied voltage in this process is considerably higher than in the cathodic processes and the amount of energy liberated at the same

Fig. 184. Current distribution in the anodic dissolution of a steel surface in an acetic acid-perchloric acid electrolyte.
total current: 0·2 amp
temperature: 20°C
solution volume: 250 ml
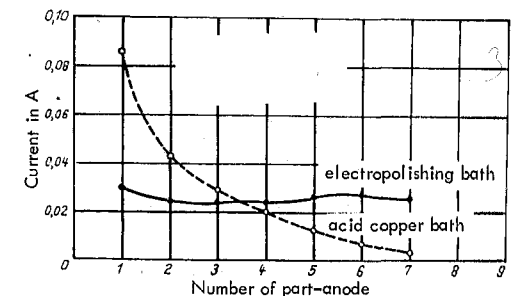
electrode area is much higher and would have led to overheating of the solution. This however did not affect the current distribution over the individual part-electrodes.·

The curve representing the current distribution is much flatter in this experiment. The part-current which flows through the individual anodes is much less affected by their distance from the cathode. In this process a film covers the anode surface which offers a high specific resistance which depends on the water and iron concentrations of the electrolyte and is much higher than that of an electrolyte layer of similar thickness. Its presence is responsible for the smoothing and brightening effect in electropolishing.

However, it is not the current distribution over the cathode or anode surface which is of importance so much as the actual thickness of metal which is deposited or dissolved at the corresponding points of the surface.

In some cases, if the metal which is deposited is not too brittle, the metal may be deposited on a Hull cell panel of stainless steel, then coated with a suitable lacquer which is allowed to dry and is pulled off the stainless steel panel together with the metal coating. The foil obtained by this means is then cut into, say, 7 sections of similar width which are placed in a solvent which removes the lacquer .coating. The metal strips are then weighed and the thickness of the deposited metal is calculated from their weight and area. This method gives very accurate results.

If it is required to investigate the influence of certain addition agents on the electrolyte, a number of Hull cells, containing solutions with varying amounts of addition agent, may be connected in series, taking care that the width and height of the areas covered by the electrolyte are the same in each case, plus a coulometer in the circuit to measure the average current passed during the experiment.

Fig. 185 demonstrates the influence of brightener addition to an acid copper plating bath on the metal distribution. Addition of brightener effects a considerable improvement in metal distribution, the improvement in coating thickness on the area furthest from the anode amounting to approximately 15 per cent.

The next illustration, Fig. 186, shows the deleterious effect on metal distribution of iron contamination in an acid copper bath. A concentration of 15 g/l iron reduces the coating thickness at the surface of the cathode furthest away from the anode by about one-third.

The brightening agents which are commonly employed in nickel plating solutions usually have little effect on metal distribution. Fig. 187 shows that the improvement in metal distribution only amounts to a few per cent. On the other hand, the metal distribution is considerably improved by altering the pH (Fig. 188). Chloride ions are also harmful to the metal distribution.
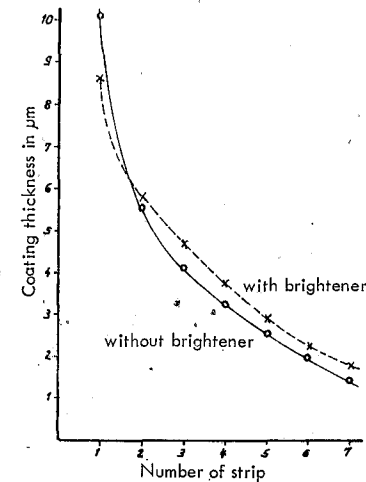
Fig. 185. Effect on metal distribution of adding brightener to an acid copper plating solution. Composition of electrolyte: 225 g/l $CuSO_4.5H_2O$ + 75 g/l H_2SO_4
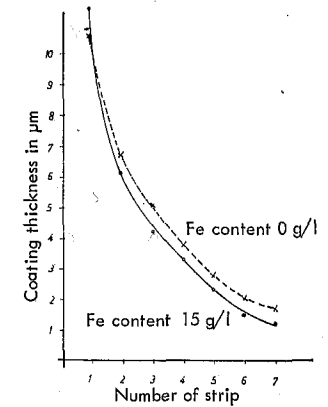
Fig. 186. Effect of the iron content in an acid copper plating solution on metal distribution.
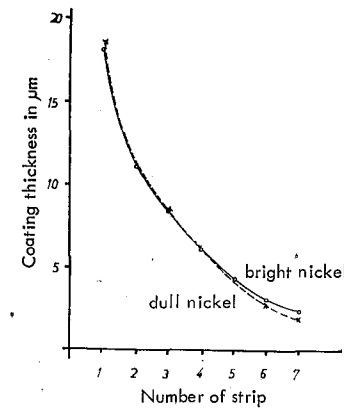
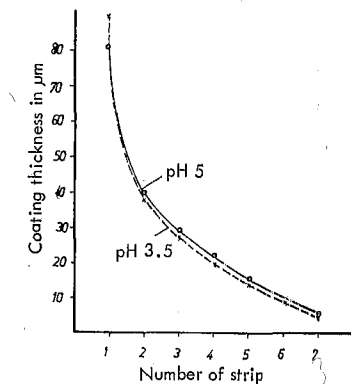Fig. 187. Effect on metal distribution of adding brightener to a dull nickel plating solution.

Dull nickel bath		Bright nickel bath	
NiSO₄.7H₂O	300 g/l	Brightener A	1·5 g/l
H₃BO₃	40 g/l	Brightener B	5 g/l
NaCl	20 g/l	wetting agent ' Sinpor'	1 g/l
Temp	55°	pH 4·5	

Fig. 188. Effect of pH on metal distribution in a bright nickel plating bath.

Dull nickel bath		Bright nickel bath	
NiSO₄.7H₂O	300 g/l	wetting agent 'Sinpor'	2 g/l
H₃BO₃	40 g/l	Brightener A	1·5 g/l
NaCl	20 g/l	Brightener B	5 g/l
Temp.	55°C	Current 1·4 amp	

An increase of from 32 g/l NaCl to 44 g/l NaCl leads to a considerable reduction in the deposition of nickel at the low current density areas of the cathode (see Fig. 189).
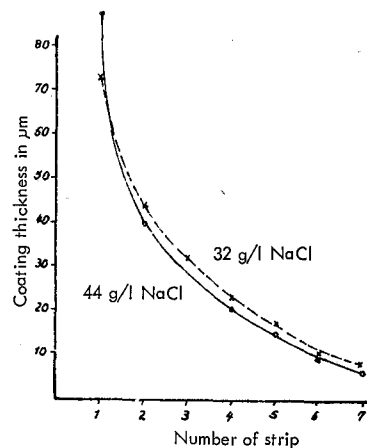

Fig. 189. Effect of chloride ion concentration on the metal distribution of a nickel plating electrolyte.

$NiSO_4.7H_2O$ 300 g/l
H_3BO_3 40 g/l
NaCl   20 g/l

If the type of metal deposited does not permit drawing off the foil from the substrate, it is possible to determine the current and metal distributions over the individual part-electrodes. In this case the part-electrodes illustrated in Fig. 181 are weighed after the experiment and, during deposition, the part-currents on the individual electrodes are noted.

Fig. 190 shows the results of such a series of experiments on a chromium plating solution. It can be seen that no chromium is deposited on the 5th to 7th electrodes. The throwing power of the chromium plating solution is known to be poor. However, the determination of the current distribution shows that even on those electrodes on which no chromium is deposited, there is an appreciable current flow which, in the present case, leads only to the discharge of hydrogen.

Fig. 190. Metal and current distributions in a chromium plating solution.
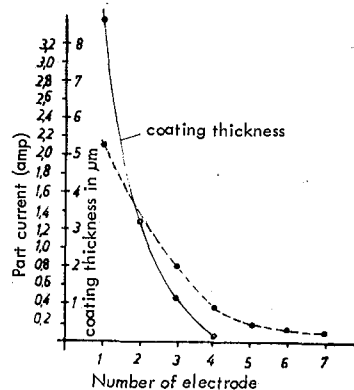
CHAPTER 12

SOME MISCELLANEOUS APPLICATIONS OF THE HULL CELL

1. Testing the suitability of basis metals

AS MENTIONED earlier, the suitability of a specific basis metal surface for receiving a certain electroplated coating can be tested in the Hull cell. This applies particularly to tests designed to evaluate the suitability of specific surface finishes.

Figs. 191 - 196 show bright nickel coatings on brass sheet panels which were first polished and then treated by brushing or grinding using abrasives of different grades. The results speak for themselves.

2. Covering power

In addition to solution control, the Hull cell may be used in a very interesting manner to determine covering power, or the lowest current density at which a deposit is produced. This application is similar to the cavity scale but the Hull cell offers the advantages of simplicity and numerical measurement of covering power.

For the purpose, it is usually convenient to plate for a given length of time, e.g. one minute, with a total current on the cathode of only 0·2 ampere. This gives a current density range from about 12 to 0·4 amp/sq ft which conveys visibly on the plate an accurate indication of the minimum covering current density as well as illustrating the remarkable effect of certain addition agents in either improving or decreasing covering power.

Important factors in such investigations are the kind of base metal and the means of its preparation, both of which are allied to the hydrogen over-voltage and deposition potential of each metal. An example of this is the influence of surface roughness upon covering power, in general an etched or otherwise roughened base metal showing different covering power than a similar polished cathode. It is therefore essential that care be exercised in selecting a uniform treatment of the base metal for determination of covering power at low current densities.

In making covering power tests, a standard surface and cleaning procedure must be used. The plating time should be the same for each set of tests. When any condition is changed the tests will vary and will be comparable only within the set.

The fact that standardisation is necessary for a covering power test indicates that variables, other than those of the plating bath, may be tested. In fact this is the case. The cleaning procedure may affect the covering power and a low current Hull test may be used to determine the best cleaning procedure.

A low current (covering power) test will readily show the effect of addition agents that improve or impair covering power. In the standard test, advantage may be taken of the fact that the back of the cathode is a low current density area. The effect of addition agents may be observed as in Fig. 197, or of variation in bath components in Fig. 198.

The effect of impurities will also readily show in this low current density area. With experience on a particular bath the back of the test plate is sometimes as informative as the front.

3. Anodic oxidation

The use of the Hull cell in investigating anodic processes has already been discussed in Chapter 11 (p. 105). It should however be pointed out that since the current flowing through an anodic oxide film is dependent on the resistance (thickness) of the film and since this thickness is dependent upon current density and time of treatment, the Hull cell scale cannot be used to read the current density directly. It is obvious that as the anodic film builds up, the distribution current will be continuously shifting until no current passes at the applied cell voltage.

Effect of Basis Metal Surface Condition
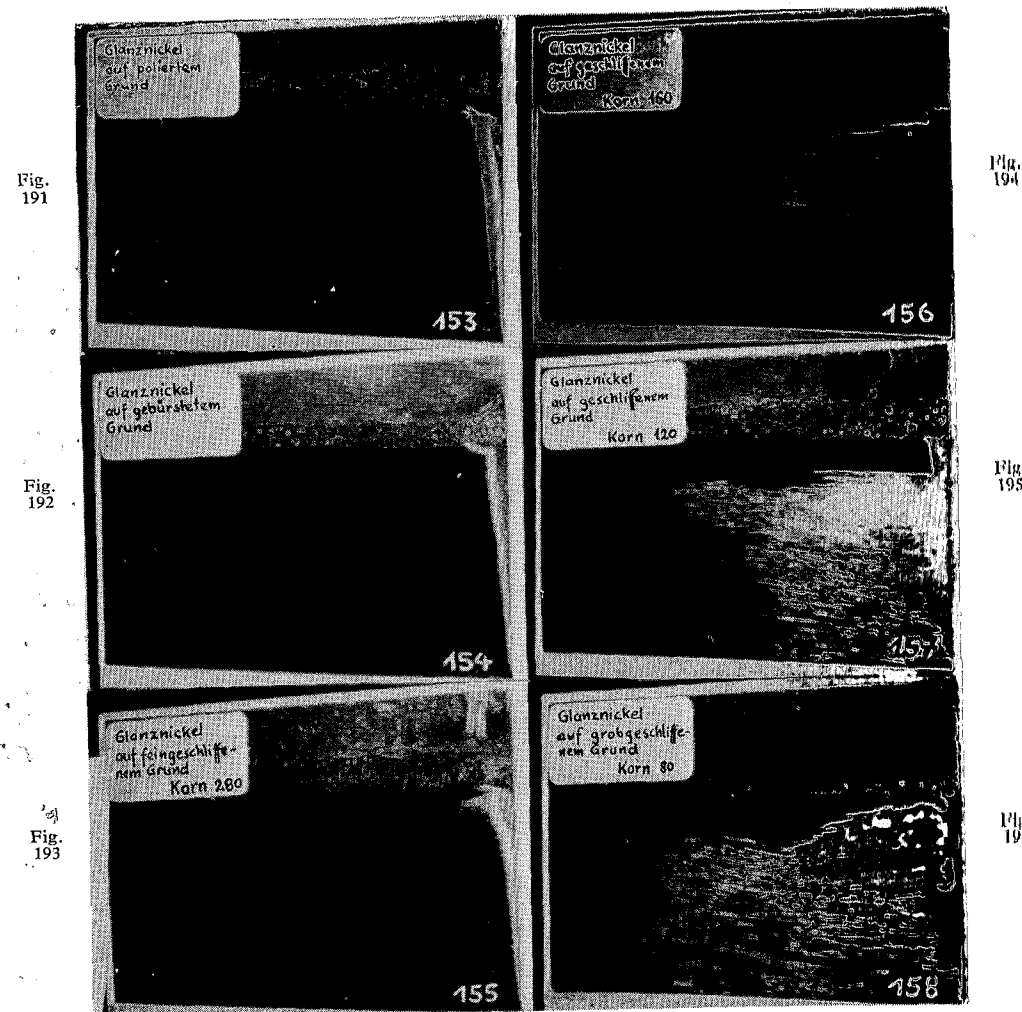
Figs. 191 - 196. Demonstrating the effect of surface finish of the basis metal on bright nickel plating. Bright nickel was plated on to polished brass panels which were : 191 : left highly polished; 192 : lightly brushed; 193 : abraded with 280 grit; 194 : abraded with 160 grit; 195 : abraded with 120 grit; 196 : abraded with 80 grit.

NO ADDITION AGENT

LOW ADDITION AGENT

OPTIMUM ADDITION AGENT

RATIO NₐCN:CᴅD = 4:1

RATIO NₐCN:CᴅD = 7:1

RATIO NₐCN:CᴅD = 10:1
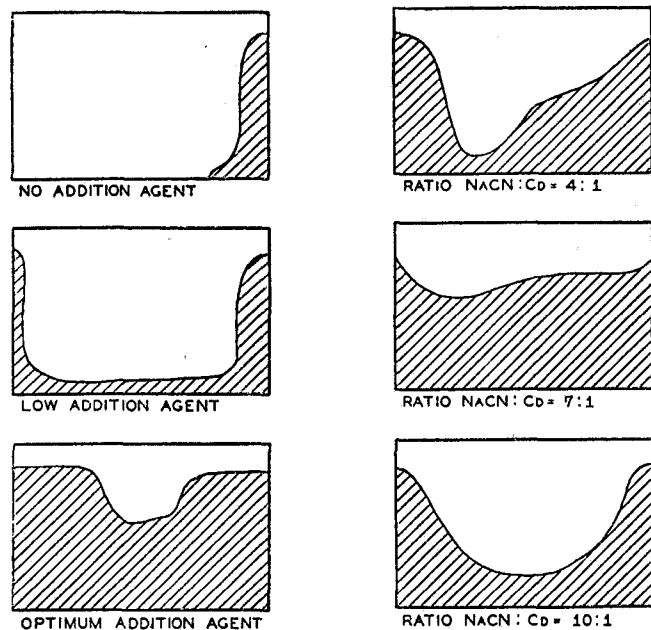
Fig. 197. Back of test plate for an acid lead bath (Sedusky and Mohler).

Fig. 198. Back of test plate for a cyanide cadmium bath (Sedusky and Mohler).

4. Electropolishing

The Hull cell has been used by Ramachandran and Jayakrishnan[*] to study the electropolishing of silverplated wire. Previously Lorking[†] had carried out Hull cell experiments regarding the effect of a few addition agents on the electropolishing of copper in phosphoric acid.

Ramachandran and Jayakrishnan silver plated copper plates $2\frac{1}{2}$ in $\times$ 4 in. in size with silver on one side (the other side having been stopped-off with a

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[*] S. Ramachandran and P. Jayakrishnan. *Electroplating and Metal Finishing*, 1966, 19, No. 3, 101 - 2.

[†] K. F. Lorking. *J. Electrochem. Soc.*, 1955, 102, 479.

lacquer) for half an hour at a current density of 5 amp/sq ft after carrying out the required preplating treatments. The plated specimens were then electropolished in a Hull cell containing 250 ml of various electropolishing solutions, with a stainless steel cathode. The cell current employed was 0·4 amp. The degree of brightness was assessed visually. Some of the Hull cell patterns obtained are shown in Fig. 199.

Bright   Semibright   Dull matt
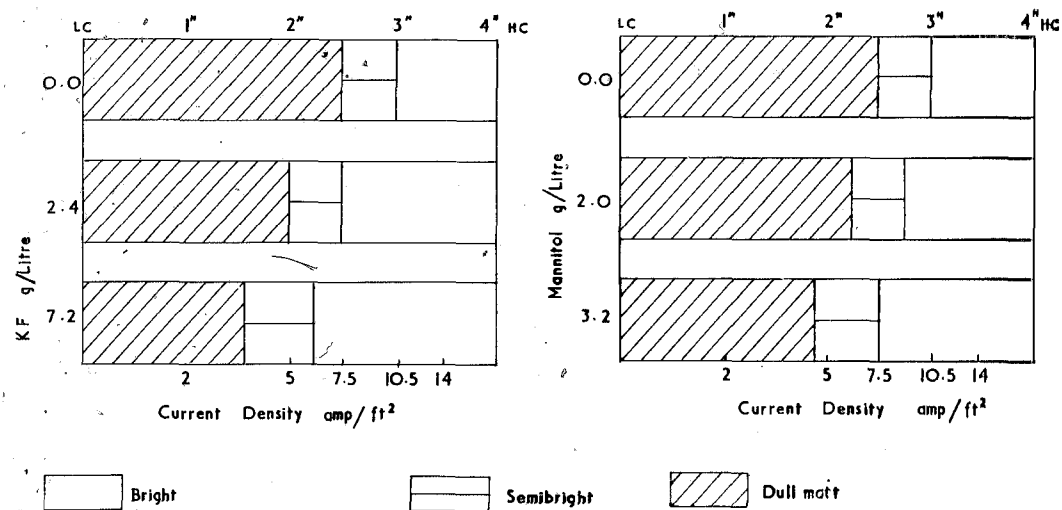
Fig. 199. Hull cell patterns and Influence of addition agents on electropolishing
L.C. = Low Current Density   H.C. = High Current Density

5. Testing tank linings

Hull cell tests were used very successfully by Edwards[*] to examine the effects of certain constituents of rubber and plastic tank linings on nickel electrodeposits. He used the 267 ml cell with an anode of rolled nickel sheet enclosed in a Terylene bag and a brass cathode which was polished, cleaned, dipped in 25 g/l sodium cyanide solution and swilled before plating. The total current in the cell was 2 amps and the plating time 15 minutes. The test panels were examined visually for colour and condition of the deposit and for the area of the cathode affected.

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[*] J. Edwards. *Electroplating and Metal Finishing*, 1957, 10, No. 2, 41 - 43.

CHAPTER 13

FURTHER NOTES ON THE USE OF THE HULL CELL

Types of anode

IN THE experiments carried out by the main author of this book, simple plate anodes were used with chromium, nickel and zinc plating solutions. The nickel anode is shown in Fig. 200. The experiments with the cadmium plating solution were undertaken with a perforated anode of the type shown in Fig. 201. A wire mesh anode was employed for the experiments with the cyanide copper plating bath and this is shown in Fig. 202. The frame of this anode consisted of 3 mm steel sheet and the copper wire was coiled on to it. The anode surface area formed in this manner is approximately 60 per cent larger than that of a simple smooth plate anode of the same size.

Incorrect polarity of the experimental apparatus

It may happen that the poles are interchanged in an experiment. Fig. 203 shows a panel produced by using the wrong electrical connections in a Hull cell test of a bright nickel plating solution. The surface of the anodically connected brass panel has undergone complete dezincification and at the low current density end of the panel the metal is a red copper colour. At the high current density end of the panel the brass is white and shows local corrosion pits. It is possible that this points to a method of testing the solubility of anodes in relation to the current density.
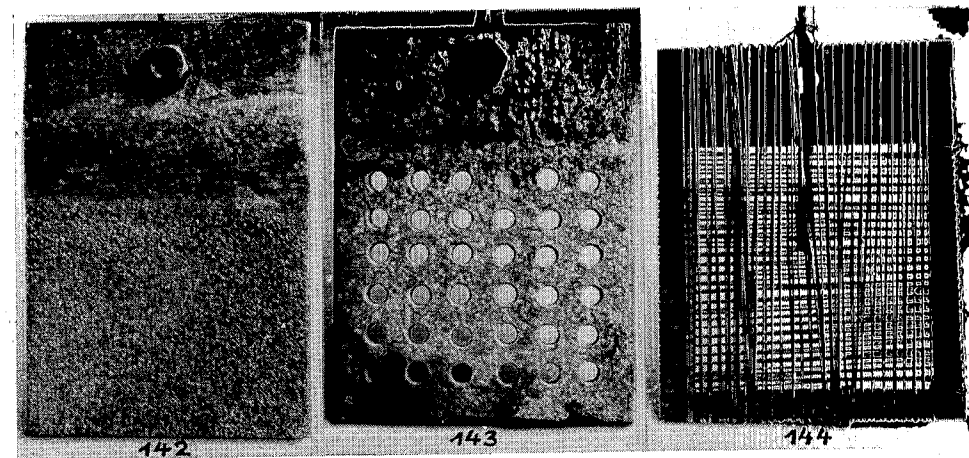
Figs. 200 - 202. Three types of anode used by the Author in his experiments. Left : sheet nickel anode. Centre : perforated cadmium anode. Right : copper anode formed by coiling copper wire on to a steel sheet.
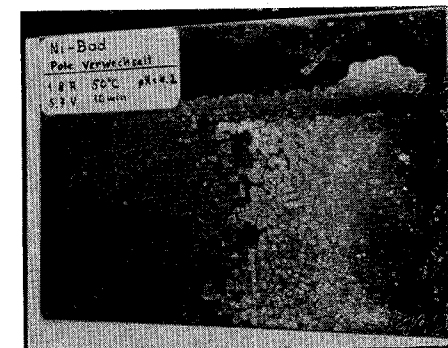
Fig. 203. Brass Hull cell test panel plated in a bright nickel plating solution using the wrong polarity.

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Hull Cell Scale Book Mark

The Hull cell scale which forms the book mark for this book has been kindly supplied by R. O. Hull & Co. Inc.

Whilst the scales which it gives for the 267, 534 and 1000 ml Hull cells apply universally, it must be remembered that the conversion factors included on the scale refer to the U.S. gallon.

1 AMP	PANEL EDGE	40	30	25	20	15	12	10	8	6	4	3	2	1	0.5
2 AMPS.		80	60	50	40	30	24	20	16	12	8	6	4	2	1
TOTAL CURRENT		AMPS./SQ. FT.—267 ML. or 534 ML. HULL CELL													

AMPS./SQ. FT.—267 ML. or 534 ML. HULL CELL
2 GM/267 ML. HULL CELL = 1 OZ./GAL. = 6.25 LBS./100 GAL.
2 ML/267 ML. HULL CELL = 0.96 FL. OZ./GAL. = 6 PTS./100 GAL.
4 GM/534 ML. HULL CELL = 1 OZ./GAL. = 6.25 LBS./100 GAL.
4ML/534 ML. HULL CELL = 0.96 FL. OZ./GAL. = 6 PTS./100 GAL.

| 3 AMPS. | | 120 | 90 | 75 | 60 | 45 | 36 | 30 | 24 | 18 | 12 | 9 | 6 | 3 | 15 |
| 5 AMPS. | | 200 | 150 | 125 | 100 | 75 | 60 | 50 | 40 | 30 | 20 | 15 | 10 | 5 | 25 |

HULL CELL SCALE

ROHCo

Symbol of Quality Metal Finishing

R. O. HULL & COMPANY, INC.
3203 W. 71st St., Cleveland, Ohio 44102
Tel: (216) 651-7300

3 AMPS.	PANEL EDGE 90	60	45	36	30	24	18	15	12	9	6	3	0.6
5 AMPS.	150	100	75	60	50	40	30	25	20	15	10	5	1

↑ TOTAL CURRENT

AMPS./SQ. FT. — 1000 ML. HULL CELL

7.5 GM/1000 ML. HULL CELL = 1 OZ./GAL. = 6.25 LBS./100 GAL.
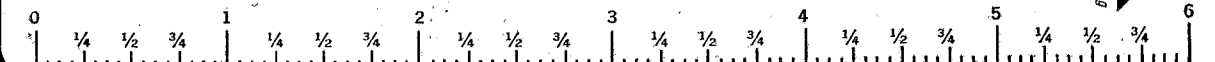7.8 ML/1000 ML. HULL CELL = 1 FL. OZ./GAL. = 6.25 PTS./100 GAL.

CU. FT. x 7.48 = GAL.
GM./L. x 0.134 = OZ./GAL.
GAL. x 3785 = ML.
LB. x 453.6 = GM.

Nothing measures up to the genuine Hull Cell test

ROHM

Symbol of Quality Metal Finishing

0   ¼ ½ ¾ 1   ¼ ½ ¾ 2   ¼ ½ ¾ 3   ¼ ½ ¾ 4   ¼ ½ ¾ 5   ¼ ½ ¾ 6