THE INFLUENCE OF THE COMPOSITION AND ACIDITY OF THE ELECTROLYTE ON THE CHARACTERISTICS OF NICKEL DEPOSITS.

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The following is an account of the third part of a general investigation into the causes and prevention of pitting in electrodeposited nickel carried out in the Research Department, Woolwich, for the Electrodeposition Research Committee of the Department of Scientific and Industrial Research.

The results of the first two parts of this investigation have been given in a previous publication.[1]   Typical examples of the defect were described and it was shown that pitting is caused by the screening effect of bubbles of gas (probably of hydrogen) which adhere to the cathode face during deposition ; the formation of hydrogen bubbles may be localised by the presence of imperfections in the surface of the basis metal and thus give rise to a variety of pitting termed " basis-metal pitting."   In the case of cathodes possessing a uniform surface, however, pitting occurs solely as a result of the condition of the solution (" solution-pitting "), and it was concluded that this type of pitting results from the presence of impurities in the solution.

In more recent investigations, however, cases of solution pitting have been observed in highly purified solutions ; the intensity of pitting and the p_H range in which it occurred were found to be influenced by the composition of the solution.   It was also observed that variations in solution composition and p_H exerted a marked effect on the hardness, microstructure, cathode efficiency and appearance of the deposits, and it became clear that the explanation of these effects could only be obtained by a systematic study of the deposits obtained under carefully controlled conditions in which the influence of the different constituents of a typical nickel depositing solution could be separately examined.   The results of this study, given in the following report, throw new light on the mechanism of nickel deposition and explain the occurrence of pitting in solutions of high purity.

PART I.   EXPERIMENTAL.

The experimental work consisted in the preparation of salts and anodes of high purity and the use of these materials in the production of deposits for comparison of the effects of changes in solution p_H and composition and the appearance, cathode efficiency, hardness and microstructure of the deposits.

[1] " The Causes and Prevention of Pitting in Electrodeposited Nickel," D. J Macnaughtan and A. W. Hothersall, *Trans. Faraday Soc.*, **24**, 497, 1928.

An endeavour was made to eliminate all sources of impurity both initially in the preparation of the materials, and also during the process of producing the deposits, when care was taken to exclude dust from the depositing solutions.   There appeared to be some doubt, however, about the effect of air dissolved in the solution ; it would appear that this might lead to the production of pits in the deposit by causing the formation of bubbles on the cathode surface.   This possibility was carefully investigated in a series of experiments in which nickel depositing solutions of composition NSB . KC (see Table II.) were saturated with air at a low temperature and were subsequently electrolysed at a higher temperature. Although a considerable number of bubbles of gas were liberated on the cathode, no increased pitting was observed.   These experiments were repeated using hydrogen instead of air with the same result.   Finally experiments were carried out in which, in one case, bubbles of air injected through a nickel gauze anode and in another case bubbles of oxygen formed by electrolysis with a platinum anode, were caused to impinge on the cathode face, but no increase in pitting was observed.

It was concluded from the above experiments that such pitting as occurs is primarily due to hydrogen gas formed at the cathode face as a result of the discharge of hydrogen ions.

Preparation of Anodes and Salts.

(a) **Preparation of Salts of High Purity.**—In view of the necessity of eliminating uncertain factors caused by the presence of impurities in the solutions, the purest salts obtainable, usually of " A.R." quality, were used, and these were in some cases further purified by treatments previously described.[2]   The analysis of the nickel salts used is given in Table I.

TABLE I.—ANALYSES OF THE NICKEL SALTS USED.

	Nickel Sulphate, $NiSO_4 . 7H_2O$.	Nickel Chloride, $NiCl_2 . 6H_2O$.
Nickel	20·8 per cent.	22·5 per cent.
Cobalt	0·09 ,,	Nil.
Iron	0·001 ,,	0·004 ,,
Zinc	0·01 ,,	0·01 ,,
Copper	0·001 ,,	trace
Manganese	< 0·001 ,,	—
Alkali metals	Nil	trace

(b) **Preparation   of   Anodes   of   High   Purity.**—Electrodeposited nickel anodes of high purity were prepared in a manner similar to that previously described [3] with the exception that a glass container with a sintered glass base was used in place of the ebonite container.

Composition of the Solutions.

In order to facilitate reference to the various solutions a scheme of lettering has been adopted in which anions and cations (other than hydrogen and hydroxyl ions) have been denoted by single letters, viz., N = nickel, S = sulphate, B = borate (in all cases added as boric acid), K = potassium, C = chloride.   Thus a solution containing nickel sulphate, boric acid and potassium chloride is referred to as NSB . KC.

[2] " The Influence of Acidity of the Electrolyte on the Structure and Hardness of Electrodeposited Nickel," D. J. Macnaughtan and R. A. F. Hammond Trans. Faraday Soc., **27**, 633, 1931.
[3] " The Hardness of Electrodeposited Nickel," D. J. Macnaughtan and A. W. Hothersall, Trans. Faraday Soc., **24**, 387, 1928.

TABLE II.—COMPOSITION OF SOLUTIONS.

Key Reference of Solution.	Grammes per Litre.				
	Nickel Sulphate, $NiSO_4 . 7H_2O.$	Nickel Chloride, $NiCl_2 . 6H_2O.$	Potassium Chloride, KCl.	Potassium Sulphate, $K_2SO_4.$	Boric Acid, $H_3BO_3.$
Solutions buffered with Boric Acid.—					
NSB . KC *	240	—	19	—	30
NSB . C	210	30·3	—	—	30
NSB . K	240	—	—	22·3	30
NSB	240	—	—	—	30
Unbuffered solutions.—					
NS . KC	240	—	19	—	—
NS . C	210	30·3	—	—	—
NS . K	240	—	—	22·3	—
NS	240	—	—	—	—

* This solution has been denoted in previous published work [2] [4] by the symbol " N."

Preparation of the Solutions.

In order that the range of acidity to be investigated in the various solutions should be as wide as possible, it was necessary to ensure that the solutions as prepared should all possess the highest p_H attainable. In the cases of solutions free from boric acid, this object was achieved by prolonged boiling of the salts dissolved in distilled water with a slight excess of highly pure nickel hydroxide suspension. The solution was then cooled, filtered and made up to volume with distilled water.

This process could not be followed in preparing the solutions containing boric acid, as on boiling such solutions hydrolysis takes place thus limiting the maximum p_H attainable to about 5·1. A special procedure was therefore adopted in which the salts and the boric acid were treated separately by boiling with pure nickel hydroxide. The solution of the salts was then allowed to become quite cold, when the hot nickel borate solution was added to it in a fine stream with constant stirring. Filtration followed by adjustment to volume completed the process.

In this way it was found possible to prepare clear solutions at p_H values considerably in excess of the true equilibrium. The solutions thus prepared were, however, found to be unstable and tended to become turbid owing to the precipitation of basic material with consequent fall in p_H even at normal temperatures. Particular difficulty was encountered in preparing solutions NSB, NSB . K and NSB . C at a high p_H for this reason.

Experimental Procedure.

Two separate series of deposits were produced (1) thin deposits for visual examination, (2) thick deposits for hardness tests and examination of microstructure ; the cathode efficiency of nickel deposition was measured in all cases and for this purpose a copper coulometer was connected in series with the nickel bath, the coulometer cathode being of such a size as to maintain copper deposition at a current density of 10 amps. per sq. ft.

1. **Thin Deposits for Visual Examination.**—The solutions, 5 litres in volume, were contained in round glass jars, 8 inches in diameter, and were heated to a temperature of 35° ± 1·0° C. A single nickel anode, approximately $4\frac{1}{2} \times 2$ inches in size, prepared as described, was suspended

in the solution. In the case of the solutions free from chloride it was found necessary to surround the anode with a porous pot which was filled with solution to which had been added an excess of pure nickel hydroxide suspension, as otherwise the low anode efficiency effected a rapid change in the p_H of the solution. Cylindrical porous pots were employed and were first ignited at a bright red heat in a muffle furnace and subsequently soaked in successive quantities of distilled water until the soluble matter had been entirely removed (as revealed by the absence of residue on evaporation of a sample of the water to dryness).

The cathodes consisted of thin copper sheets, $1\frac{1}{4} \times 2$ inches in size. They were carefully cleaned and copper coated in an acid copper sulphate solution to a thickness of 0·0005 inch. They were then washed, dried and weighed and subsequently prepared for deposition by cathodic treatment for a few seconds in an alkaline solution followed by a momentary dip in 10 per cent. sulphuric acid solution—a procedure which did not involve any appreciable change of weight.[4]

One cathode was used in each experiment and was arranged at right angles to the plane of the anode so as to secure an equal distribution of current on each face.

The p_H value of the solutions was reduced in stages by the addition of pure sulphuric acid, the acidity being maintained within $\pm$ 0·05 p_H units of the stated values in the case of the buffered solutions, and within $\pm$ 0·1 p_H units (approximately) in the case of the unbuffered solutions, any upward tendency being corrected by the addition of acid. Duplicate deposits were made at each p_H value, the intervals of p_H between successive stages being determined partly by the ease with which the p_H could be controlled and partly by the degree to which change in p_H was expected, from preliminary observations, to alter the characteristics of the deposits.

Other conditions of deposition were as follows :—

Cathode current density 11 amps. per sq. ft. (1·2 amps./sq. dm.).
Duration of deposition 2 hours (equivalent to a thickness of deposit of approx. 0·0015 in. (0·04 mm.)).

On removal from the solution the cathodes were rinsed in distilled water followed by alcohol, dried in an air oven at 80° C., cooled and weighed.

2. Thick Deposits for Hardness Testing and Micro-examination.—This part of the work was confined to the buffered solutions containing boric acid, since the p_H of the unbuffered solutions could not be controlled sufficiently closely throughout the prolonged period of deposition necessary to produce a thickness of deposit adequate for Brinell hardness testing.

The solutions were contained in round glass jars supported in a thermostatically controlled water bath, four purified nickel anodes hung on nickel wires being arranged symmetrically around the internal periphery of the jars. Three litres of solution were used in the case of NSB . KC and NSB . C and 5 litres in the case of NSB . K and NSB.

The cathodes which were hung centrally in the jars, consisted of pieces of hexagonal mild steel rod which had previously been coated with a layer of electrodeposited copper ·001 inch in thickness. The cathodes measured 1·5 inch in length and 0·625 inch across the flats in the case of solutions NSB . KC and NSB . C, and 1·125 inch in length and 0·25 inch across the flats in the case of solutions NSB . K and NSB, the smaller size being employed in conjunction with a larger volume of solution in order to minimise changes of acidity by reducing the amount of current flowing in relation to the volume of solution. The cathodes were prepared for deposition by the method previously described.

[4] " The Influence of Small Amounts of Chromic Acid and Chromium Sulphate on the Electrodeposition of Nickel," D. J. Macnaughtan and R. A. F. Hammond, *Trans. Faraday Soc.*, **26**, 481, 1930.

The p_H of the solutions was reduced in stages by the addition of sulphuric acid, duplicate deposits being prepared at each stage, except in cases where increasing acidity during deposition rendered the preparation of exact duplicates impossible.

On removal from the bath the deposits were washed, dried, weighed, and then lightly polished, and tested for hardness by the Brinell method using a 1 mm. ball and 10 kg. load.

For examination of the microstructure the deposits were afterwards thickly coated with electrodeposited copper and cut transversely near the centre, the sections thus obtained being ground and polished.

Control of Acidity.

Frequent determinations of the solution p_H were made in all experiments by the colorimetric method using buffer standards, the accuracy of which had been checked. The results obtained were subsequently corrected to allow for the salt error, the required correction having been separately determined for each solution over the whole p_H range in which it was operated by quinhydrone electrode measurements. The corrected values are given throughout the report. In all the solutions studied, the colorimetric method was found to give a result approximately 0·5 p_H units higher than the quinhydrone electrode value in the range p_H 3·0 upwards.

In the case of solutions NSB . KC and NSB . C the p_H tended to rise during deposition and the acidity could be kept constant to within close limits by the addition of sulphuric acid as required. In the case of solutions NSB . K and NSB, however, the solution p_H tended to fall owing to low anode efficiency due to the absence of chloride. This was especially marked in the p_H range in which the solutions were poorly buffered, viz., p_H 5·5 − 3·5 approximately, and in the case of deposits prepared within this range, the acidity of the solution varied appreciably between the commencement and finish of the run.

In these cases an arbitrary p_H value was taken for the purposes of plotting the curves, which assumed the effective p_H to lie at a point two-thirds of the way downwards from the commencing to the finishing values. The shape of the curves subsequently obtained justified this assumption.

The conditions of deposition are summarised as follows :—

Temperature of the solutions	.	$35° \pm \frac{1}{2}°$ C.
Cathode Current Density .	.	11 Amps./sq. ft.
		(1·2 Amps./sq. dm.).
Duration of Deposition	.	24 hours.

(equivalent to a thickness of deposit of approximately 0·014 inches (0·35 mm.)).

Buffer Characteristics of Solutions.

The buffering properties of each solution were determined over the range of p_H investigated by titrating 2 litre samples prepared as described above with 2N . H_2SO_4. Typical curves are shown in Fig. 1.

Experimental Results.

Visual Examination of Deposits.

The results of cathode efficiency determinations are shown graphically in Figs. 2 and 3 ; the deposits from each solution were arranged in order of decreasing p_H and their appearance as regards pitting, and brightness was then summarised and is recorded diagrammatically in the panels in Figs. 2 and 3, the same p_H scale applying to both the curves and the panels.

(1) **Summary of Observations relating to the Occurrence of Pitting.** —Pitting occurred to some extent in all the solutions investigated with the possible exception of NS . K.   Pitting was not observed in the lustrous mirror-bright deposits, nor in general on deposits produced at a p_H lower than 3·0 except in the case of solution NS . C in which pitting occurred at p_H values as low as 2·6.   In two solutions, NSB, NSB . K, minute pits barely visible to the naked eye were formed below p_H 3·0, and from p_H 2·5 downwards there was a tendency for vertical streaks to
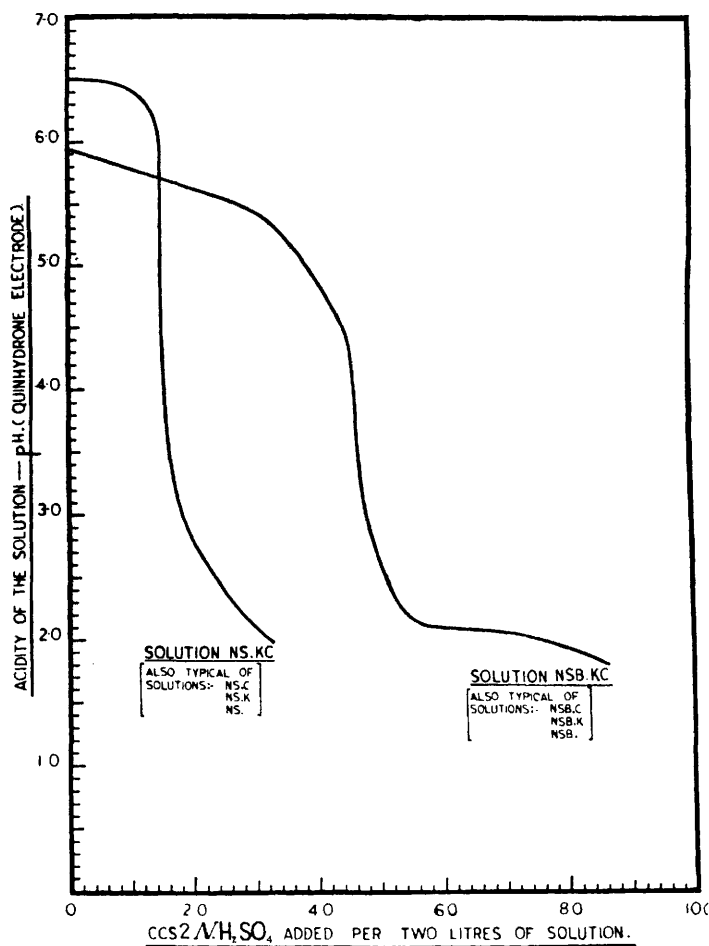

FIG. 1.—Buffer characteristics of the solutions used.

emanate from these minute pits.   This type of streak, frequently referred to as a " gas-streak " has previously been described.[1]

The eight solutions may be conveniently divided into three groups according to the intensity of pitting.   Thus deposits from solutions NSB, NSB . C, NS . C were severely pitted.   None of these solutions contain potassium, whilst two contain chloride.   Deposits from solutions NSB . KC and NS . KC, each of which contain both potassium and chloride, were slightly pitted.   Deposits from solutions NSB . K, NS . K and NS which do not contain chloride were slightly or not pitted.

Pitting in each solution commenced and ceased, in general, at well-defined acidities and attained a maximum intensity at an intermediate p_H. In one case, *viz.*, NS, there appeared to be two unconnected ranges of acidity in which pitting occurred.
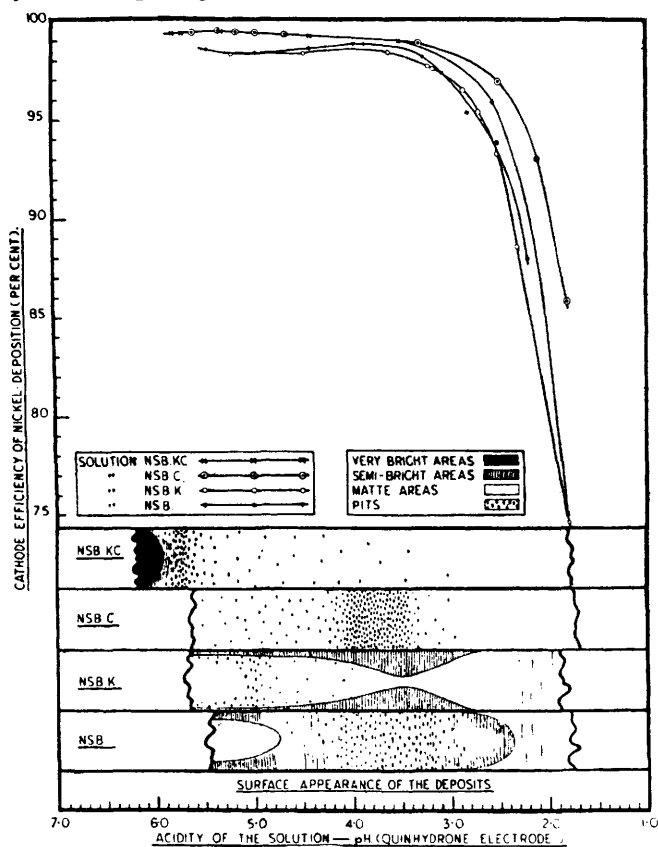

FIG. 2.—Cathode efficiency / p_H curves and effect of solution p_H on pitting and appearance of deposits.   Buffered solutions (containing boric acid).

The p_H ranges in which pitting occurred in the various solutions are summarised in Table III.

TABLE III.—OCCURRENCE OF PITTING IN RELATION TO SOLUTION p_H.

Solution.	p Range in which Pitting Occurred.	p_H at which Maximum Intensity of Pitting was Observed.
NSB	4·7 — 2·5	3·3
NSB . C	5·6 — 3·0	4·0 Severely
NS . C	6·3 — 3·0	(i) 6·3 pitted
		(ii) 3·3
NSB . KC	5·9 — 3·0	5·75 Slightly
NS . KC	5·8 — 3·5	5·8 — 4·5 pitted
NS	(i) 6·0	—
	(ii) 3·5	— Very slightly
NS . K	3·0 — 3·5	— or not pitted
NSB . K	5·65 — 4·3	5·0

Although pitting was not observed in mirror-bright deposits, it was found that a slight change in the conditions of deposition which caused an alteration in appearance from bright to matt also frequently resulted in the production of pitting. Thus, a slight downward displacement of p_H in solution NSB . KC in the neighbourhood of p_H 5·9 effected a change from a semi-bright unpitted, to a matt and severely pitted deposit ; occasionally both matt and bright areas were obtained on a single deposit owing to irregular current distribution, and in such cases pitting was generally concentrated in the matt areas immediately adjacent to the bright zones.
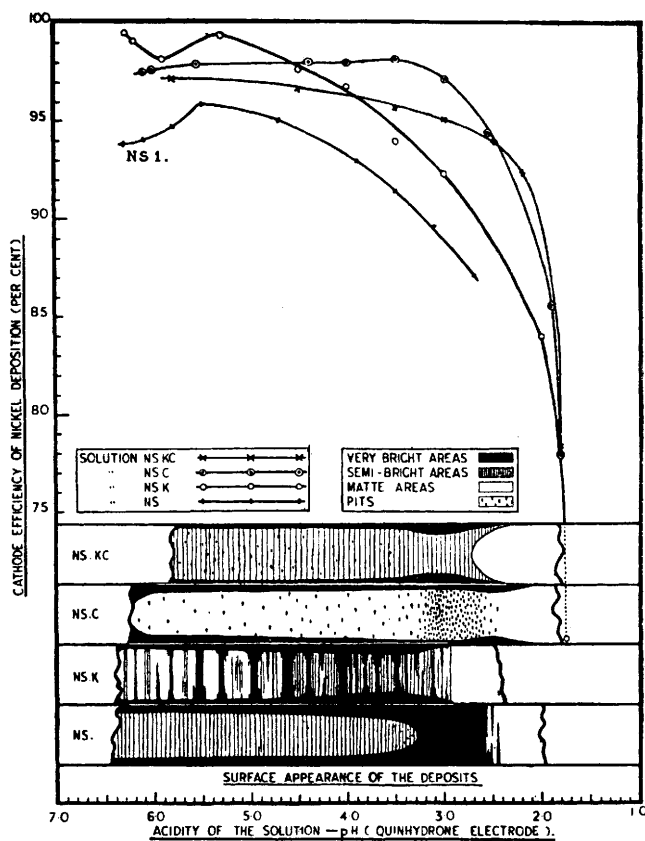

FIG. 3.—Cathode efficiency / p_H curves and effect of solution p_H on pitting and appearance of deposits.   Unbuffered solutions.

(2) **Summary of Observations relating to Surface Brightness of Deposits.**—In general, the deposits from the buffered solutions containing boric acid were matt and crystalline whilst those from the unbuffered solutions tended to be lustrous or mirror bright.

Bright deposits were, however, obtained in certain conditions from the buffered solutions ; thus in the presence of chloride, the deposits were bright only in a very restricted range towards the upper p_H limit, but in the absence of chloride there was a tendency for brightness to occur at p_H values intermediate between the highest and lowest p_H values studied. This effect was especially pronounced in solution NSB.   At all other p_H values investigated matt deposits were produced in the buffered solutions.
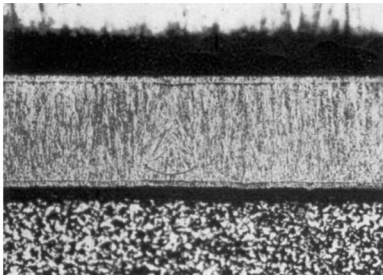
FIG. 4.—Markings suggesting the presence of a partially ruptured film at the cathode surface during deposition. (Solution NS . K, p_H 3.5.) (× 2)
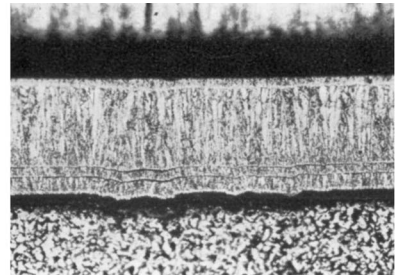

FIG. 5.—Exfoliated deposit prepared in solution NS . K, p_H 3·3 (cf. Fig. 4). The deposit prepared under similar conditions at p_H 3·0 was sound and matt. (× 2)
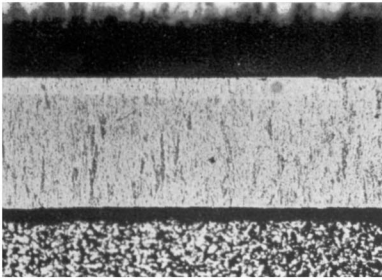
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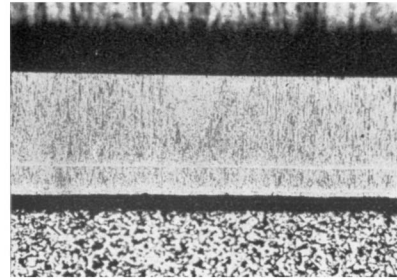p_H 5·45.   Brinell No. 221. p_H 4·95.   Brinell No. 177.
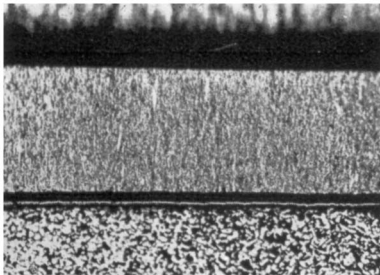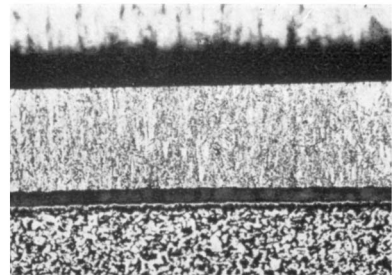
p_H 4·4.   Brinell No. 251. p_H 3·85.   Brinell No. 273.

p_H 2·8.   Brinell No. 218. p_H 2·2.   Brinell No. 174.

FIG. 9.—Influence of solution p_H on the microstructure of the deposits (× 55).   (Solution NSB.)

[*See page* 740.

Deposits from the unbuffered solutions were in general lustrous or mirror-bright and frequently streaky. Solution NSC was an exception, the majority of deposits from this solution being matt. As in the buffered solutions a tendency was observed for maximum brightness in the chloride-free solutions to occur at an intermediate point in the p_H range. Thus it was found that there was a greater tendency for bright deposits to be produced in solutions free from chloride than in corresponding solutions in which chloride was present, this being true of both the buffered and unbuffered groups of solution. In all the solutions, sound matt deposits were obtained at the lowest p_H values investigated. Thus in solution NS . K. at p_H 4·0, the deposits were almost entirely bright. At p_H 3·5 mirror-bright markings resembling the pattern of watered silk appeared on the deposit, suggesting the presence of a partially ruptured film at the cathode surface during deposition (see Fig. 4), and at a slightly lower p_H the deposits became seriously exfoliated (see Fig. 5). A marked change took place at about p_H 3·0 when the deposits became sound and matt with only an occasional bright streak. Below this p_H, matt deposits were obtained to the end of the series.

Cathode Efficiency Results.

1. **Buffered Solutions containing Boric Acid.**—The cathode efficiency/p_H curves shown in Fig. 2 are of the same general form for all the solutions studied; the cathode efficiency remained approximately constant with change of acidity until p_H 3·5 was reached, when it commenced to fall at a rate which increased rapidly with further decrease in p_H.

In the case of both of the solutions free from chloride (*viz.*, solutions NSB and NSB . K), the cathode efficiency curves lie below those relating to the solutions containing chloride, the presence of Cl′ apparently favouring an increase in the cathode efficiency.

Comparison of the curves obtained for solutions NSB . KC and NSB . C suggests that the presence of alkali metal favours a more rapid decline in the cathode efficiency below p_H 3·5.

FIG. 6.—Different cathode efficiency / p_H curves obtained with three similar nickel sulphate solutions (NS).

Thus increase in cathode efficiency may result either from (*a*) the presence of chloride, or (*b*) the absence of potassium in solutions of the type at present under discussion.

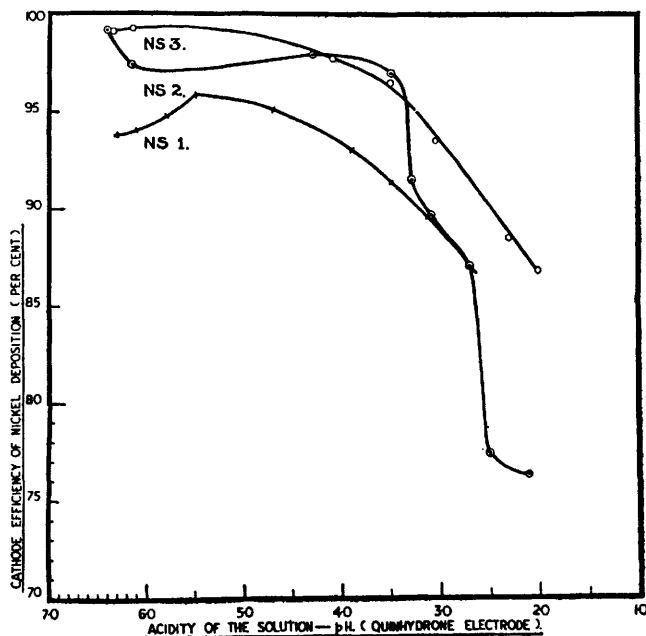The results of cathode efficiency measurements made in conjunction

with the preparation of the thick deposits for hardness testing agreed almost exactly with those previously obtained for thin deposits and shown in Fig. 2.

2. Unbuffered Solutions.—The cathode efficiency/p_H curves for these solutions are shown in Fig. 3.

As in the case of the buffered solutions, reduction of the solution p_H was in general accompanied by a lowering of the cathode efficiency. In solutions NS . C and NS . K, the fall in cathode efficiency was preceded by a slight rise whilst this initial rise was marked in the case of solution NS . 1.

The cathode efficiency figures obtained for solution NS . K were somewhat irregular, particularly in the high p_H range, as indicated by the inflection in the curve between the initial p_H and p_H 5·3.
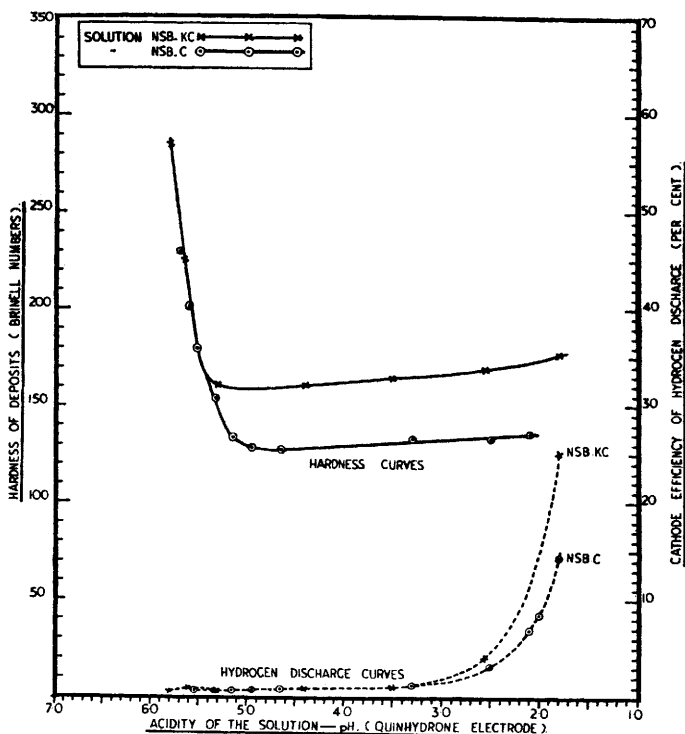

FIG. 7.—Hardness / p_H curves—hardening effect of potassium in presence of chloride ions.   (Solutions NSB . KC and NSB . C.)

This irregularity was observed to a greater extent in solution NS as is clearly shown by Fig. 6 in which curves are given showing the cathode efficiency/p_H relationship for three separate nickel sulphate solutions of identical composition, *viz.*, NS . 1, NS . 2 and NS . 3 ; it appears to be associated with the absence of chloride and may be indicative of the presence of gelatinous films at the cathode face as discussed later. The relatively low cathode efficiency figures obtained in solution NS . 1 together with the initial steep rise of the curve with decrease in p_H are especially suggestive of such film formation, progressive rupturing of the film probably accounting for the rising cathode efficiency at the commencement of the curve.

Over a large part of the p_H range investigated, the curves for the solutions containing chloride (*viz.*, NS . KC and NS . C) lie above those relating

to the chloride-free solutions. This conforms with the result described above for the buffered solutions.

Comparison of the curves obtained for solutions NS . KC and NS . C and those obtained for solutions NS . K and NS . I suggests that when chloride is present, the presence of alkali metal causes a reduction in the cathode efficiency, whilst in solutions free from chloride, the presence of alkali metal favours an increase in cathode efficiency. These results are partially confirmed in the case of the buffered solutions described above.

A study of the cathode efficiency/p_H curves reveals that in general, for equal conditions of solution p_H, higher cathode efficiency is obtained in the buffered solutions than in the unbuffered solutions, and that the
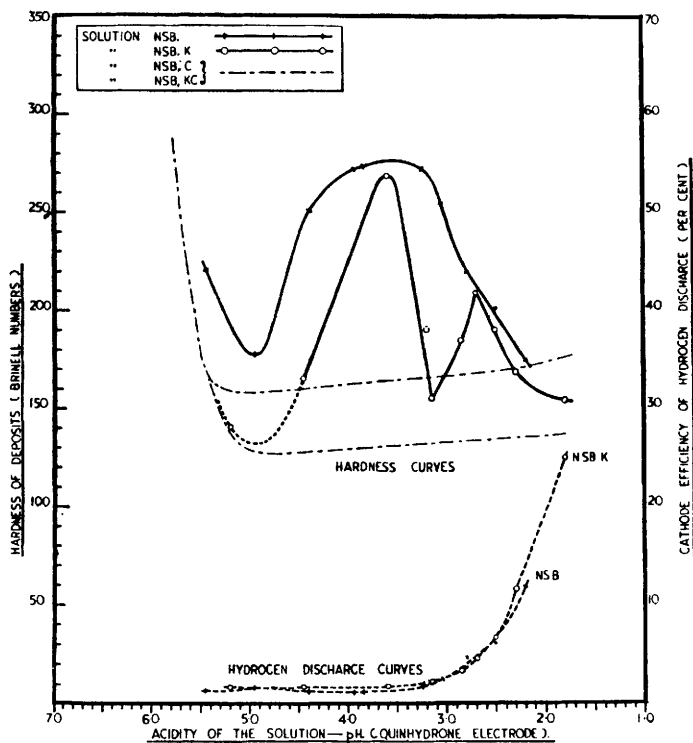
FIG. 8.—Hardness / p_H curves—effect of absence of chloride ions. (Solutions NSB and NSB . K.)

cathode efficiency falls off more rapidly in the unbuffered solutions than in the buffered solutions.

Hardness of Deposits.

The results obtained are illustrated graphically in Figs. 7 and 8 which show the relationship between bath acidity and the hardness of the deposits.

It was found impossible to prepare solution NSB . K in a condition less acid than p_H 5·2. Had this been possible, it is considered that an initial rapid fall in hardness from a high commencing value, corresponding to the first stage of the curve for the NSB . KC solution would have been obtained. The probable course of the curve for this solution above the actual commencing p_H, is therefore indicated by a dotted line in Fig. 8.

With this exception deposits of high hardness were produced in all cases from the solutions at the highest p_H values used, and in every case, the hardness diminished rapidly with decrease in p_H until a critical p_H value was reached at which the abrupt fall in hardness with further lowering of p_H ceased. Below this point, the hardness/p_H relationship was found to differ in the various solutions with the presence or absence of chloride and to a lesser extent of potassium ions. In the case of the two solutions containing chloride ions (NSB . KC and NSB . C), reduction in p_H below the critical point produced relatively little change in hardness ; although in these two solutions the hardness was similar above the critical point, the deposits obtained from the solution containing potassium (NSB . KC) were appreciably and consistently harder below the critical point than those produced from the solution free from potassium (NSB . C). The hardness figures obtained from the solutions free from the chloride ion (NSB . K and NSB) showed a marked rise in hardness with decrease in p_H below the critical point up to a well-defined maximum, after which further decrease in p_H resulted in a diminution in hardness, the deposits from the NSB solution becoming progressively softer, whilst those from the NSB . K solution, after an initial fall, rose in hardness to a second but lower maximum and then became progressively softer ; the solution containing potassium (NSB . K) in this case yielded somewhat softer deposits than were obtained in the absence of this ion (NSB solution).

Visual examination of the deposits showed that variation in solution p_H produced the same general change in the characteristics of the deposits as was observed in the thin deposits, the appearance of which has been described above. The change in appearance of the deposits with alteration in p_H was in close agreement with what would be expected from the results of the hardness measurements, *i.e.*, the harder deposits tended to be of a lustrous and the softer deposits of a matt appearance. Micro-examination showed that in all cases, the grain size of the hard and lustrous deposits was small but that as the hardness diminished and the deposits became more matt in texture, the grain size increased. This correlation between grain size, surface smoothness and hardness is confirmatory of previously published results.

Photographs showing the microstructure of the deposits obtained in NSB solution are given in Fig. 9.

PART II.   DISCUSSION OF RESULTS.

1. Hardness of Electrodeposited Nickel.

In the discussion of the results of a previous investigation [2] in which solutions containing both potassium and chloride ions were employed, it was considered that, whereas the rapid rise in hardness with increase in p_H above the critical p_H could be best explained as due to an effect of basic material formed at the cathode face in modifying the size of the crystals, below this critical p_H the slight rise in hardness which was found to occur with decrease in p_H might be considered to be due to a direct effect of the increasing amount of hydrogen which is simultaneously discharged with the metal, although this was considered unlikely.

In the present investigation the additional data obtained with respect to the variation of hardness and cathode efficiency with p_H throws considerable doubt on the possible relationship between the amount of hydrogen discharged and the properties of the deposit.

Thus, comparison of the hardness figures obtained from the NSB . KC and the NSB . C solutions shows that the absence of potassium results in the production of appreciably softer deposits below the critical p_H,

whereas although the amount of hydrogen discharged is less in the solution giving the softer deposits, this difference is relatively slight.

n the case of the solutions from which chloride is absent, the disparity between the hydrogen discharged and the hardness of the deposit becomes even more marked. Thus in solutions NSB . K and NSB decrease in p_H below the critical value results in a substantial increase in hardness to a maximum followed by a decrease (see Fig. 8). No corresponding change in the amount of hydrogen discharged occurs, however.

It would thus appear that it is not possible to relate the properties of the deposit to the amount of hydrogen discharged, and in view of the pronounced effect on the characteristics of nickel deposits produced by the precipitation of basic hydroxides in the film of liquid adjacent to the cathode when the solution p_H is high, it becomes of importance to consider the degree to which this factor also operates to increase hardness when the solution p_H is low.

The Formation of Basic Material at the Cathode.

The electrochemical discharge of nickel ions at the cathode is always accompanied by the discharge of hydrogen ions. As there is no evidence that any other electrode process takes place at the cathode, the deviation of the efficiency of nickel deposition from 100 per cent. is therefore the measure of the extent of hydrogen discharge. This removal of hydrogen ions from the liquid adjacent to the cathode in relatively stagnant solutions decreases the acidity compared with that of the bulk of the solution and in consequence a gradient of decreasing acidity is formed from the adjacent solution to the cathode face.

In order to understand fully the reactions which occur at the cathode whereby basic material is formed, it would be necessary to know precisely the composition and p_H of the film of liquid at the cathode face. There is no known method whereby this information may be obtained. It has, however, been established by the results of this investigation together with those of the supplementary investigation on the effect of annealing on the deposits * that basic material is present in deposits formed in the various solutions over the whole range of p_H studied. It may therefore be concluded that the film of liquid immediately adjacent to the cathode must at least reach the precipitation p_H of the basic salt.

Assuming that it does not exceed this p_H, then the film of liquid adjacent to the cathode is at a constant p_H no matter what is the p_H of the bulk of the solution. This is likely since any tendency to rise in p_H would be checked by further precipitation. If this is the case then the change of efficiency which is found to occur at different p_H values of the solution would appear to be related to changes in the amount of hydrogen discharge which is required to bring the liquid continuously arriving at the cathode face to the precipitation point. It is, however, also necessary to explain the various amounts of basic material which are co-deposited at different acidities as revealed by the differences in hardness of the deposits and by micro-examination of the deposits after annealing *in vacuo* as shown in the supplementary investigation.*

It is only possible to conjecture as to the manner in which this may take place. Thus (1) the film of liquid at the cathode face may not be

* See following paper, p. 755.

maintained continuously at the precipitation p_H but may fluctuate between this and a lower value. In this case the amount of basic material would vary with changes in the proportion of the time during which the solution was at the precipitation p_H. This explanation involves periodic phenomena at the cathode face such as has been considered likely to occur on other grounds by various investigators ; (2) the film of liquid may be continuously maintained at the precipitation p_H but the thickness of the film may vary. In this case the thicker the film of liquid at the precipitation p_H the greater the amount of basic material that is available for co-deposition with the nickel and the greater the hardness of the deposit.

Whatever view is finally established as correct the following question then arises : why should there be a rise in hardness as the p_H is decreased below the critical p_H in the case of deposits from all solutions and especially in the solution free from chloride ions in which this rise is very great ?

Some indication of the relative amounts of basic material likely to be present at the cathode face during deposition from similar solutions at different acidities may be obtained in the following manner. From the efficiency of hydrogen ion discharge in each case, the weight of hydrogen discharged by unit current in unit time is calculated and from this the equivalent volume of standard acid is deduced. The volume of standard acid necessary to change the p_H of 1 c.c. of the solution from the precipitation point of nickel hydroxide to the acidity under consideration may be read off from the buffering curve (Fig. 1). The removal of a mass of hydrogen ions equivalent to this volume of standard acid from 1 c.c. of the solution would reduce it to the precipitation point. Hence by proportion the volume of solution brought to the precipitation point by the removal of the calculated amount of acid can be found.

The results of calculations made in this manner, for two typical solutions are shown graphically in Fig. 10. As calculated it appears that in both solutions, above a certain p_H (e.g. NSB . C solution p_H 5·3, NSB solution p_H 4·0) there is a rise in the amount of basic material, while below this p_H there is first of all a slow and then finally a rapid rise. Fair agreement between the relative amount of basic material formed and the hardness of the deposit occurs above the critical p_H. At lower p_H values, however, the rapid rise in the amount of basic material occurs at a p_H value considerably lower than the rise in hardness of deposits from NSB solution to which it might be expected to correspond. There is, however, an assumption made which is likely to affect the actual shapes of the curves. The calculations are based upon the experimentally determined values for the buffering properties of the bulk of the solution whereas it is really the buffer properties of the cathode film which are involved. There is reason to believe that the solution adjacent to the cathode face is much more dilute than the bulk liquid owing to discharge of nickel ions and the repulsion of anions from the cathode face (this is discussed later). The repulsion will be greatest on the trivalent borate ions so that the composition of the liquid adjacent to the cathode face will, in the case of both of the solutions under discussion, approach that of a dilute solution of nickel sulphate (with and without the presence of chloride ions in the two cases respectively). When the results of calculations for such a solution (e.g. NS . K) are plotted the curve takes the form shown dotted in Fig. 10.

If, now, the variation in the calculated amounts of basic material which tends to form with changes in p_H of the bulk solution is compared

with the changes in hardness with p_H, it is seen that there is a fair correspondence in the case of the NSB solution except that as the p_H is lowered below 3·0 there is a progressive drop in hardness. This divergence may be explicable, in view of the changed conditions at lower p_H values. Thus as the p_H of the bulk solution is decreased below p_H 3·0, the solution at the cathode face becomes subjected to increased agitation by rising hydrogen bubbles owing to the greater amount of hydrogen which is discharged. In consequence there may be a decreasing
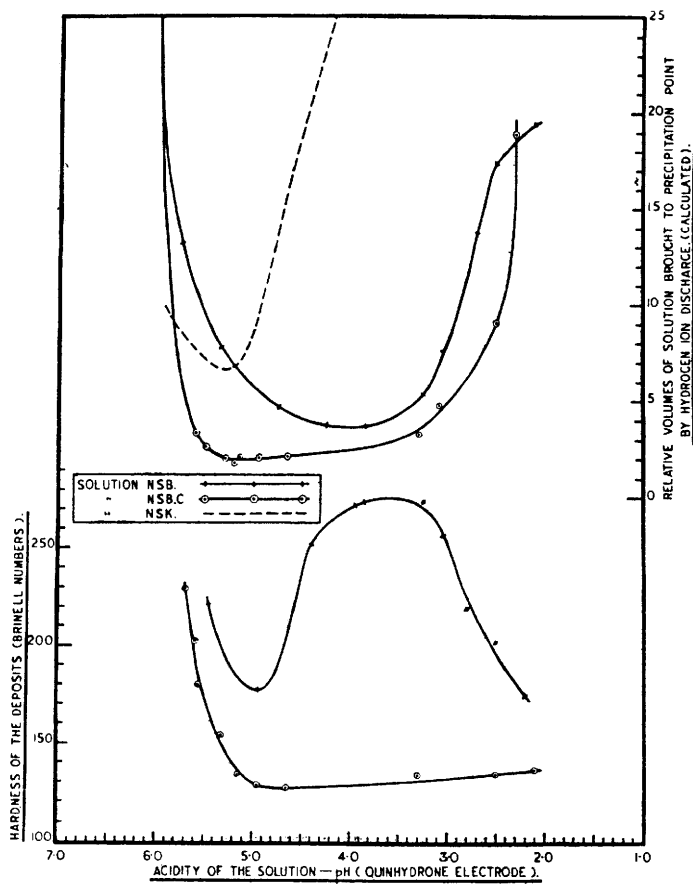

FIG. 10.—Comparison between change in hardness of nickel deposits (lower curves) and the possible variation in amount of basic material produced at the cathode surface (upper curves) with alteration in solution p_H.

tendency of the solution at the cathode face to rise in p_H to the precipitation p_H since the effect of the hydrogen discharge will be distributed over a greater quantity of solution. It would thus appear that in the NSB solution there are grounds for concluding that the variation in the tendency for basic material to form with change in p_H of the bulk solution is similar to the variation in hardness. On the other hand in the p_H range below the critical p_H there is not the same degree of relationship in the case of the NSB . C solution which differs from the NSB solution in containing chloride ions.

Significance of Basic Material in Relation to Hardness.

(a) **Amount of Basic Material.**—The fact that the calculations referred to above indicate that there is a similar rise in the amount of basic material produced at the cathode face in the p_H range below the critical p_H irrespective of the presence of chloride in the solution, whereas there is a striking difference in the effect of p_H on the hardness, might appear to raise doubts as to any direct relationship between hardness and the amount of basic material. The difference cannot be explained as due to difference in the effects of agitation of the solution at the cathode surface in this range of p_H since the cathode efficiencies are similar.

Similarly, the omission of the potassium ion from the NSB . KC solution does not affect the calculated amount of basic material produced over a considerable p_H range (*viz.*, p_H 5·5 — 3·5) although it produces a marked difference in hardness of deposits formed in this p_H range.

Although it would thus appear that the differences in hardness observed cannot be directly related to the amount of basic material produced, this possibility cannot be entirely disregarded in view of the difficulty at present of making proper allowance for all the factors concerned, as for example the effect of the chloride and potassium ions on the buffer characteristics of the cathode film.

There are, however, reasons for concluding that these constituents are likely to have an important effect on the nature of the basic material which would appear to afford an adequate explanation of the experimental results.

(b) **Nature of Basic Material.**—The effect on the characteristics of the deposit produced by basic material precipitated in the film of liquid adjacent to the cathode is likely to vary considerably according to whether the material is present in the colloidal or in the flocculated condition.

The pronounced effect of colloidal matter on the structure and properties of electrodeposits is well known. In the case of a positively charged sol such as nickel hydroxide sol for example, the material is attracted towards the cathode face where it becomes discharged together with the nickel ions. The inclusion of hydroxide, or more probably oxide (as there will be a pronounced tendency for the combined water to be removed into the solution at the moment of discharge) in the deposit in this way interferes with the normal process of crystal formation and results in a small grain size and an increased hardness.

A neutral precipitate in the neighbourhood of the cathode, however, is not likely to have any appreciable direct influence on the structure of the deposit, especially if it becomes dispersed in the solution (as is likely, due to convection and agitation effects, in the neighbourhood of the cathode) when in normal conditions it would be rapidly dissolved. An indirect effect, may, however, be produced by such a precipitate and this will be discussed later.

Experiments have shown that if nickel hydroxide sol is added to any of the solutions under consideration immediate precipitation occurs provided the solution is sufficiently high in p_H not to redissolve the hydroxide ; the precipitation is due to rapid discharge of the positively charged sol by the negatively charged anions which are present in high concentration. From investigations on nickel hydroxide sols [5] it may be

[5] " On the Preparation of Colloidal Solutions of Nickel and Cobalt Hydroxides and some other compounds of these Metals," O. F. Tower, and M. C. Cooke, *J. Physic., Chem.*, **26,** 728, 1922.

concluded that if anions are present in even moderate concentration right up to the cathode face, any basic material formed is likely to be in the condition of a neutral precipitate.

The Influence of Potassium and Chloride Ions on the Amount and Nature of the Basic Material.

In the electrolysis of nickel depositing solutions of the type studied in this investigation, it is unlikely that conditions exist which entirely preclude the formation of nickel hydroxide sol.   Thus during electrolysis there is a general repulsion of the negative anions in the solution by the negatively charged cathode and attraction of these anions towards the positively charged anode.   The migration rate is slow and the drift of anions is opposed by diffusion, agitation and convection together with the tendency of such cations as are approaching the cathode to drag along with them an atmosphere of negative anions.   There will thus always be likely to be a certain concentration of anions in the liquid relatively close to the cathode face.   The concentration will, however, fall off as the cathode face is actually approached since the force of electrostatic repulsion will become very large as the distance is decreased to a small value.   It is thus likely that in the thin film of liquid immediately adjacent to the cathode face the concentration of anions will drop to zero.   As the discharge of hydrogen which results in the solution rising in p_H towards the precipitation point * occurs at the cathode, it will be in the inner layer of liquid close to the cathode face that the precipitation point will be reached.   It is thus likely that here nickel hydroxide will form in colloidal condition and being positively charged will be attracted to the cathode where it will tend to interfere with crystal growth, i.e., will influence the hardness and properties of the deposit.   If, however, the amount of solution which is brought to the precipitation p_H extends beyond the inner layer, which alone is free from anions, then flocculation of the sol is likely to occur in the outer layers with the production of an uncharged precipitate (probably a basic precipitate of nickel hydroxide + anion).   Owing to its electrically neutral character this precipitate will not be electrically attracted to the cathode face and is thus less likely to exert a direct effect on the properties of the deposit.

It would thus appear that any factors which tend to diminish the thickness of the liquid layer in which colloidal nickel hydroxide can be formed will tend to diminish interference of the growth of crystals by the presence of colloidal matter, i.e., will tend to encourage the formation of larger crystals and softer deposits.   It might be expected that this effect is likely to arise from the presence of chloride ions in the solution. These ions are smaller than the sulphate ions and as they have the same kinetic energy their diffusibility is greater.   Also they carry only one negative charge while the sulphate ions carry two.   There will thus be less tendency for the chloride ions to migrate away from the cathode zone during the passage of current.   More important still, they will be able to approach closer to the cathode face than the sulphate ions. Thus it would appear that the zone sufficiently free from anions to allow

* The term " precipitation point " is used to indicate the minimum p_H value at which nickel hydroxide can be present in either a colloidal or a flocculated condition.

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the precipitated basic material to be retained in the sol form, will be decreased when chloride ions are present in the solution.

The effect of chloride ions would thus tend to encourage the formation of softer deposits as has been found in the low p_H range under consideration.

If the effect of the presence of chloride ions is as described above then the hardening effect of potassium ions in solutions also containing chloride ions might be anticipated owing to the known stabilising action of potassium on positively charged colloid sols. Thus it has been found in a number of investigations that a greater concentration of anions is required to cause the flocculation of an inorganic sol when there is also present in considerable concentration cations likely to stabilise the sol. It was concluded by Tower [5, 6] for example, that potassium ions tend to stabilise the nickel hydroxide sol. In consequence, if potassium ions are present in the liquid adjacent to the cathode face a greater thickness of liquid may reach the precipitation p_H with the resulting formation of sol, before the zone is reached in which the concentration of chloride ions is sufficiently high to more than counter-balance the stabilising effect of the potassium ions. This implies that of the basic material which is formed a greater proportion will tend to remain in the sol form if potassium ions are present and in consequence the deposit will tend to be harder. That potassium ions will concentrate in the liquid film adjacent to the cathode face is inevitable since the positively charged potassium ions are not only highly diffusible but are electrostatically attracted to the cathode, and as they are not discharged they will tend to reach a relatively high concentration. This would explain the difference observed in the p_H range below the critical p_H between solution NSB . KC containing potassium ions and the NSB . C solution not containing potassium ions.

It has been found, however, that in the absence of chloride ions, the presence of potassium, in the range of p_H under consideration, causes a softening of the deposit which might appear to throw doubt on the explanation suggested above.

There is, however, experimental evidence to show that the flocculated precipitate may have a pronounced indirect effect upon the hardness of the deposit by influencing the relative rates of arrival of nickel and hydrogen ions to the cathode face, and that it is due to the modifying influence of the potassium ions on this indirect effect that the contradictory effect of potassium in non-chloride solutions is explained.

The Indirect Effect of Flocculated Basic Material on the Conditions at the Cathode Face.

Flocculated basic material, if present in a loose form in which it is easily dispersed and dissolved in the bulk of the solution, is not likely to exert any appreciable effect on the structure of the deposit or on the cathode efficiency. If, however, the material is precipitated in a condition such that it is not readily dispersed, it may have a pronounced indirect effect on the characteristics on the deposit. For example, it may be precipitated in the form of a membrane which is selectively permeable to nickel and hydrogen ions, allowing the smaller and more

[6] " Note on Colloidal Nickel Hydroxide," O. F. Tower, *J. Physic. Chem.*, **28**, 176, 1924.

mobile hydrogen ion to pass in preference to the nickel ion. Under these conditions there will be an increase in the rate of discharge of hydrogen, *i.e.*, a fall in cathode efficiency. As a consequence of this, the average p_H of the film of liquid between the membranous precipitate and the cathode will rise so that there will be a greater tendency for the formation of basic material. As this increased amount of basic material is produced in the film of liquid relatively free from flocculating anions there will be more sol produced ; the increase in the amount of sol coupled with the decrease in concentration of nickel ions will tend to increase the hardness of the deposit.

The effect described above is likely to vary in degree with the structure and thickness of the film, both of which will be considerably influenced by the buffering properties of the solution and by the presence of stabilising cations such as potassium or flocculating anions such as chloride ; the structure of the film will be considerably influenced by a number of complex factors which determine its rate of flocculation. If the structure of film is sufficiently coarse, without being readily dispersible, its selectively permeable properties will be destroyed and the material will then function merely as an obstruction to the free movement of solution in the neighbourhood of the cathode and there will thus be less opportunity for convection and diffusion to effect dispersion of the more alkaline solution adjacent to the cathode. This will tend to reduce the hydrogen ion concentration of this liquid and increase the concentration of sol thus giving rise to a higher cathode efficiency and an increased hardness, although the effects produced in this way might be expected to be much less pronounced than in the case of the selectively permeable membrane.

The production of a dense membrane such as would be selectively permeable to different ions is more likely to occur in relatively unbuffered solutions where even a small hydrogen discharge will cause a rapid rise in p_H of the liquid adjacent to the cathode.

Definite evidence of the production of such a precipitate was observed during the formation of deposits in some of the solutions free from boric acid. Thus in the nickel sulphate solution (NS) in a certain range of p_H, sheath-like films were formed which became detached from the cathode and were then clearly visible. A similar effect but to a slighter degree was observed in the nickel sulphate solution containing potassium sulphate (NS . K). Indirect evidence of the presence of such films was obtained in the results of cathode efficiency measurements in the unbuffered solutions (*cf.* p 738). Reference to Fig. 3 shows that the cathode efficiency in a nickel sulphate solution NS is lower over the whole range of p_H tested than in the NSB . KC solution. Yet it would appear that in the more highly buffered solution, the hydrogen ion concentration of the film of liquid adjacent to the cathode should be higher than in a poorly buffered solution and that the cathode efficiency should in consequence be less. That this is the case in certain circumstances can be shown by the lowering in cathode efficiency produced by a considerable increase in the buffering properties of the NSB . KC solution by the addition of 50 g. per litre of sodium acetate. The explanation of this anomaly is obtained if the film of precipitate is acting as a selectively permeable membrane in the manner already discussed.

On the addition of potassium sulphate to the nickel sulphate solution, the cathode efficiency over the whole range of p_H is increased. It is still not so high, however, in the lower p_H ranges as in the better buffered

NSB . K solution.   On the reasoning given above, there is still some restriction to the approach of nickel ions to the cathode face, but the effect is less than in the nickel sulphate solution owing to the stabilising action of the potassium ions in reducing the amount of basic material precipitated.

The introduction of chloride into the unbuffered solutions exerts a marked effect on the cathode efficiency and on the formation of an obstructive membrane.   Thus reference to Fig. 3 shows that the cathode efficiency is higher over a wide range of p_H in solutions NS . C and NS . KC than in corresponding solutions free from chloride.   This is consistent with the experimental observation of the difficulty of obtaining visible films from the chloride solutions.   It was in fact found necessary to raise solution NS . C to an abnormally high p_H in order to get any visible evidence of film formation whereas, as indicated above, films were seen in solution NS over a wide range of p_H.   This difference would appear to be due to the effect of chloride ions on the physical condition of the flocculated basic material in rendering it more easily dispersed and dissolved in the bulk of the solution and so minimising the tendency to film formation.

In the case of the buffered solutions the p_H of the solution near the cathode is likely to be somewhat lower owing to the better buffering properties of the solution and there will not in consequence be as great a tendency for the production of a dense film.   At the same time, over the whole p_H range, the cathode efficiency in solutions free from Cl' is lower than in similar solutions containing Cl' ;   this is consistent with the existence of a film in solutions free from chloride which is to some extent selectively permeable and which would therefore operate to reduce cathode efficiency and increase hardness in the manner already described. In these solutions, the presence of potassium, by its stabilising action on the sol will somewhat reduce the effectiveness of the film as a selectively permeable membrane and its action in this respect would appear, from the fact that it results in a somewhat lower hardness, to more than counterbalance the effect of the increased amount of sol.

It is necessary, however, to emphasise that these marked differences between the two types of solution may be modified both at higher and at lower p_H numbers than the range under consideration.   As the p_H is lowered there will be an increasing tendency for the precipitate produced in the non-chloride solution to be dissolved so that marked differences in the rates of solubility of the precipitated material will tend to disappear.   This is consistent with the fact that at low p_H, the hardness of deposits from both types of solution tends to approximate to a similar low value.

At higher p_H than the range under consideration the fact that the hardness is less influenced by the presence of chloride ions may be due to the fact that the p_H of the liquid adjacent to the cathode face is reaching a value at which the solubility of the basic chloride is diminished. This effect may explain why in practically all the solutions the hardness curves tend to approximate to similar values above the critical p_H. In these circumstances the solutions containing chloride ions will tend to produce a greater amount of obstructive material at the cathode face, which, by its indirect action in causing the p_H of the cathode film to rise in the manner previously discussed, will have a hardening effect on the deposits ;   this may more than counterbalance the softening effect ordinarily attributable to the chloride ion.

2. Pitting.

Examination of the deposits obtained in the course of this investigation, the results of which are indicated pictorially in Figs. 2 and 3, shows that pitting occurs in the case of most of the solutions in certain ranges of p_H. In view of the fact that care was taken by suitable preparation of the cathodes to exclude the possibility of basis metal pitting, and that materials of high purity were employed, it would appear that solution pitting does not necessarily result from the presence of impurities, as was previously suggested.[1]

Of the solutions which have been examined, only two are of practical importance—*viz.*, NSB . KC and NSB . C. As the occurrence of pitting in solutions of this type has been studied by other investigators, it is of importance to consider these previous observations in relation to the present results.

Discussion of Previous Work on the Relation between Pitting and Solution p_H.

Thompson,[7] and later Montillon and Cassel,[8] examined the effect of solution p_H on the tendency to pitting in a solution very similar to the NSB . KC solution and concluded that pitting was most likely to occur with reduction in p_H below p_H 4·0. This conclusion is contrary to the results found in the present investigation since it was found that pitting was entirely absent in this solution below p_H 3·0 while a marked tendency to pitting was observed in high p_H ranges. This discrepancy is probably due either to the confusion between basis metal pitting and solution pitting by previous investigators or to their use of insufficiently pure materials.

Kreuger and Foerster [9] working with a solution similar to NSB . C found that pitting disappeared with reduction in p_H below a certain value. This is in general consistent with the results obtained in the course of the present work although the actual p_H value below which Kreuger and Foerster found pitting to cease is somewhat higher.

Hydrogen Discharge in Relation to Pitting.

The facts that pitting is due to the screening effect of hydrogen bubbles and that the amount of hydrogen discharged is increased with decrease in solution p_H are largely responsible for the popular assumption that pitting should be increased with decrease in solution p_H. Examination of a large number of deposits of different thicknesses formed on cathodes free from surface imperfections and in solutions prepared from highly purified chemicals has shown, however, that the reverse is actually the case, and that pitting may be eliminated by the use of a sufficiently low p_H, whereas it is liable to occur at higher p_H values.

Examination of a magnified image of the cathode during nickel deposition using the apparatus described in the previous report [1] has shown that in the low p_H range in which the deposits were found to be unpitted, hydrogen bubbles appeared in large numbers over the surface of the

[7] " The Acidity of Nickel Depositing Solutions," M. R. Thompson, *J. Amer. Electrochem. Soc.*, **41**, 333, 1922.

[8] " Acidity of Cobalt and Nickel Plating Baths," G. H. Montillon and N. S. Cassel, *J. Amer. Electrochem. Soc.*, **45**, 259, 1924.

[9] " The Behaviour of Nickel Anodes," F. Foerster and F. Kreuger, *Z. Elektrochem.*, **33**, 406-425, 1927.

cathode ;   these, however, in general became quickly detached when only small in size.   On the other hand in the higher p_H range, although fewer bubbles were generally produced, they tended to remain longer in contact with the cathode and to grow to a larger size before becoming detached.

A relatively rapid rate of hydrogen discharge would appear to favour decreased pitting in at least two ways : (a) There is a more rapid growth of hydrogen bubbles relative to the rate of increase in thickness of the deposit.   In consequence the depressions formed will be shallower and will be less effective in holding the bubbles in position in the period during which they are growing to the size at which buoyancy finally causes their detachment; (b) The greater amount of agitation set up by the more rapid bubble discharge will tend to produce dislodgement of the bubbles at an earlier stage.

These factors, while possibly accounting in the main for the greater freedom from pitting at low solution p_H, are clearly inadequate to explain all the results obtained from the two solutions of practical importance previously referred to.   Thus, very serious pitting was found in deposits produced from the NSB . C solution in the p_H range 4·2 — 3·4, whereas pitting in this p_H range in the NSB . KC solution was only very slight ; yet in this p_H range the rate of hydrogen discharge, as evidenced by cathode efficiency measurements was found to be identical in the two solutions.   Further, with increase of p_H above 4·2 in the NSB . C solution, pitting becomes less pronounced, although conditions should favour a slower growth of hydrogen bubbles and less agitation at the cathode face.

It would thus appear that factors other than those directly connected with the rate of hydrogen discharge are operating to affect the degree of bubble adhesion.

Basic Material in Relation to Pitting.

Foerster and Kreuger [9] suggested that the presence of nickel hydroxide at the cathode face has an important bearing on the degree of pitting in the higher p_H ranges in which they found this defect to be most pre-valent, and they quote experiments in which a visible precipitate was observed to coat the bubbles as a membrane and to retard their detach-ment from the cathode.

Although no visible precipitated matter has been observed surround-ing the bubble walls in any of the present experiments with the NSB . C solution (which is similar to that used by Kreuger and Foerster), there would appear to be a number of reasons to account for increased bubble adhesion caused by the presence of basic material formed at the cathode face ;   and since it has already been shown that the evidence of hardness measurements points to the presence of this material in the solution adjacent to the cathode (either in a colloidal or flocculated condition), it becomes of considerable importance to examine the possible effect of basic material on pitting.

i. Colloidal Basic Material.—Colloidal basic material formed at the cathode during nickel deposition is positively charged and has been considered [10, 11] to increase the adhesion of bubbles to the negatively

[10] " Mechanically Perfect Electrolytic Nickel," C. P. Madsen, J. Amer. Electrochem. Soc., **45**, 249, 1924.
[11] " The Commercial Deposition of Nickel," E. J. Dobbs, J. Electroplaters' and Depositors' Tech. Soc., **2**, 1927.

polarised cathode if present in the bubble interface. The reduction in pitting with reduction in p_H in the NSB . KC solution might appear to favour this view, since pronounced pitting occurs under conditions which, as shown by the high hardness of the deposits, favour the presence of a relatively large amount of colloidal matter at the cathode face. With a small reduction in p_H, however, the tendency to pitting becomes only slight, whereas the hardness is still high.

Furthermore, no satisfactory relationship between colloidal material and pitting would appear to be possible in the case of the NSB . C solution. In this solution, the amount of colloidal matter present at the cathode face (as evidenced by the hardness of the deposits), is practically constant over the p_H range $5 \cdot 0 - 2 \cdot 0$, although marked changes in the tendency to pitting occur in this range. Also the deposits formed in this p_H range from the NSB . C solution are appreciably softer (indicating less colloidal matter) than those from the NSB . KC solution, although they are considerably more pitted.

2. Flocculated Basic Material.—It is well known that the stability of foams is increased by the presence of finely divided material in the bubble interface, and this fact was probably the basis of Kreuger and Foerster's suggestion that a membrane of precipitated hydroxide was causing the bubbles to adhere to the cathode face. It does not, however, appear to be necessary that the flocculated material should surround the bubble. In the case of a vertically arranged cathode, the maximum stress on the bubble wall tending to cause its detachment will be in the nature of tension on the underside of the bubble at its junction with the cathode face. An accumulation of finely divided precipitate around the base of the bubble will thus tend to prevent its detachment by increasing its rigidity in the region of maximum stress; attraction of this basic material to the cathode by surface forces may also tend to increase the adhesion of the bubble.

It would thus appear that the adhesion of a bubble to the cathode will be increased by the presence of flocculated material around the area of contact of the bubble and the cathode, and that it is therefore unnecessary for the flocculated matter to be present in visible quantity. Since the zone of liquid in which flocculated material is most effective in promoting adhesion of the bubbles is close to the cathode surface, it will tend to remain high in p_H and so prevent solution of the flocculated matter even when the bulk of the liquid is at relatively low p_H (especially as the solution immediately surrounding the bubble will be comparatively stationary and unaffected by the general upward streaming of liquid over the cathode). Furthermore, the quantity of basic material around the base of the bubble, and hence the amount of flocculated matter and the adhesion of the bubble, will tend to be augmented by prolonged contact of the bubble with the cathode owing to the screening from agitation and diffusion; this will tend to result in the solution adjacent to the bubble rising to an abnormally high p_H. It is significant in this connection to observe that traces of precipitated matter are frequently found in pits and on the rim of the lower side of the pit, and that certain pits have black interiors (this is particularly characteristic of those formed in the NSB . C solution in the p_H range $4 \cdot 2 - 3 \cdot 4$) suggesting that partial reduction of the basic material has taken place.

The experimental evidence, summarised pictorially in Figs. 2 and 3, is in close agreement with the explanation of solution pitting in pure solutions in terms of flocculated basic material at the cathode face.

Thus in the NSB . C solution, pitting occurs in maximum intensity in the p_H range 4·2 — 3·4, which is the range in which an increased amount of basic material would be expected to be formed from the results of hardness tests in the NSB solution (see Fig. 8). The addition of chloride to the NSB solution (converting it into the NSB . C solution) causes flocculation of the colloidal matter, thus converting it into a form which does not effect hardness but which has a marked influence in promoting pitting.

Further evidence of marked pitting when flocculated basic material is likely to be high is shown in the corresponding solutions free from boric acid, *viz.*, NS . C and NS. In solution NS the maximum hardness, as indicated by the degree of brightness of the deposits, occurs in the p_H range 3·3 — 2·6. An increased quantity of basic material is therefore to be expected in this range. Upon the addition of chloride to the solution (converting it into NS . C) there will therefore be a maximum amount of flocculated basic material, and this occurs in the p_H range in which pitting was found to be at a maximum.

Corroboration of the above hypothesis is also obtained on consideration of the effect of alkali metal and alkaline earth metal ions on pitting.

Effect of Alkali Metal and Magnesium Ions on Pitting.

1. Potassium.—The presence of potassium was found to have a pronounced effect in decreasing the amount of pitting.

This effect is particularly marked in the range p_H 4·2 — 3·4 in buffered solutions containing chloride and is also apparent in the range p_H 3·2 — 2·6 in the unbuffered solution containing chloride, as shown by comparison of the deposits from the NSB . KC and NSB . C solutions (Fig. 2) and the NS . KC and NS . C solutions (Fig. 3). (See also results shown in Table IV.) This may be explained by the reduction in the amount of flocculated matter due to the stabilising action of the potassium ion in the manner already discussed.

In buffered solutions free from chloride the presence of potassium also results in a decrease in the amount of pitting in the low p_H range by diminishing the quantity of basic material flocculated by the sulphate ions. In the unbuffered solutions free from chloride, the potassium would appear to function in a similar manner although the amount of pitting was only slight in its absence.

The presence of potassium thus results in a striking reduction in the intensity of pitting in a variety of solutions, and this is consistent with its action in stabilising the colloid at the cathode face and thus reducing the degree to which flocculation occurs.

2. Sodium, Lithium, Ammonium and Magnesium.—A study was made of the effect on susceptibility to pitting of the addition of sodium lithium, ammonium and magnesium chlorides respectively to NSB solution. The results which are given in Table IV. show that the alkali metal ions, sodium and lithium, tend to diminish pitting appreciably, whilst negligible effects are produced by ammonium and magnesium.

These results give additional support to the view that the amount of flocculated matter present at the cathode face exerts an important action in increasing the adhesion of hydrogen bubbles since the effectiveness of potassium, sodium and lithium in stabilising certain inorganic sols against flocculation by chloride and sulphate ions would be expected to be greater than that of magnesium and ammonium.

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TABLE IV.—INFLUENCE OF ALKALI METALS AND MAGNESIUM IONS ON PITTING.

The chloride additions referred to in this table were made to NSB *solution, the sulphate additions to* NSB. C *solution.*

Cation Added.	Amount Added (g. per litre).	Prevalence of Pitting.	p_H Range Examined.
(as Chloride). Nickel, (NiCl$_2$6H$_2$O) Potassium, (KCl) Sodium, (NaCl) Lithium, (LiCl) Ammonium, (NH$_4$Cl) Magnesium, (MgCl$_2$6H$_2$O)	Equivalent to 19 g./l. potassium chloride.	Severe pitting. Very slight pitting. Very slight pitting. Slight pitting more than with potassium. Severe pitting. Severe pitting.	5·5 — 3·0 5·5 — 3·0 5·5 — 3·0 5·5 — 3·0 5·5 — 3·0 5·5 — 3·0
Potassium sulphate, (K$_2$SO$_4$)	0·05 g./l. 0·15 g./l. 0·35 g./l. 0·75 g./l.	Severe pitting. Severe pitting. Slight pitting. Very slight pitting.	p_H 3·6 only. p_H 3·6 only. p_H 3·6 only. p_H 3·6 only.

Summary and Conclusions.

The cathode efficiency, surface appearance (particularly as regards pits), and Brinell hardness of nickel deposits prepared at various acidities from a group of solutions each consisting of nickel sulphate together with one or more of the following substances : boric acid, potassium sulphate, potassium chloride, nickel chloride—have been examined ; materials of high purity were used for the preparation of the deposits. The results have been summarised graphically and pictorially.

Deposits of high hardness were produced in all cases examined from the solutions at high p_H, and reduction in solution p_H effected a rapid reduction in hardness until a critical value was reached at which the abrupt fall in hardness with further lowering in p_H ceased. Below this point the hardness p_H relationship was found to vary in the different solutions according to the presence or absence of chloride and to a lesser extent of potassium ions. In the solutions containing chloride, reduction in p_H below the critical p_H produced relatively little change in hardness, the solution containing potassium yielding appreciably and consistently harder deposits than that free from potassium. In solutions free from chloride, the deposits showed a marked rise in hardness with decrease in p_H below the critical point up to a well-defined maximum, after which further decrease in p_H resulted in a diminution in hardness ; in this case the solution containing potassium yielded somewhat softer deposits than were obtained in the absence of that ion. The results indicate that no direct relationship between hardness and the amount of hydrogen discharged can be established ; the suggestion previously advanced that basic material precipitated in the liquid adjacent to the cathode face is responsible for the hardness of nickel deposits is substantiated and elaborated.

By calculation from the buffering properties of the solution and the cathode efficiency it is shown that the depletion of hydrogen ions from the liquid adjacent to the cathode may result in an increasing amount of basic material being present at the cathode face as the p_H is decreased. It is considered that the basic material is initially formed in the colloidal state and is positively charged. In this state it migrates to the cathode and, by inclusion on the crystal faces, restrains crystal growth, causing the formation of a fine grained and hard deposit.

In the presence of negatively charged anions, however, the colloidal material tends to be discharged and flocculated ; the resulting neutral precipitate may have no effect on the deposit owing to its being swept into the bulk of the solution and there dissolved, or it may exert an indirect effect by remaining in the proximity of the cathode as an obstructive or even semi-permeable membrane. It is considered probable that chloride ions have a greater flocculating effect than sulphate ions owing to their closer approach to the cathode, whilst the presence of potassium ions will tend to oppose the flocculation.

In the absence of chloride ions there is evidence, from the observation of films upon the cathode and from cathode efficiency figures, that the flocculated precipitate obstructs the free movement of the solution and thus favours the formation of a greater amount of colloidal material ; the obstructive nature of the precipitate is diminished in the presence of potassium, and this more than counterbalances the influence produced by its stabilising effect on the colloidal material.

The manner in which these effects influence the hardness of the deposit obtained both above and below the critical p_H is discussed.

The intensity and distribution of the defect of pitting observed in the deposits obtained is recorded. It is found in general to be associated with the absence of potassium and the presence of chloride and to be dependent to a marked degree upon the acidity of the solution, being absent in all cases from deposits prepared at p_H values below 2·6 (quinhydrone). It has not been found possible to correlate the occurrence of the defect with the rate of hydrogen discharge from the cathode or with the presence of colloidal material at the cathode face.

The factor which is chiefly responsible for increasing the adhesion of bubbles to the cathode face is considered to be finely divided basic material of neutral electrical properties which is absorbed in the gas-liquid interface close to the cathode.

In agreement with this view it is found that pitting occurs to a maximum degree in each solution in the range of p_H in which the greatest quantity of flocculated matter is likely to be formed. The influence of chloride in stimulating, and potassium ions in inhibiting, the defect is thus clearly associated with the flocculating and stabilising effect respectively of these ions upon the basic material present ; the similar but lesser inhibiting effect of sodium and lithium is in agreement with this view.