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CONTROL OF ACIDITY IN NICKEL DEPOSITION

I. INTRODUCTION

The present investigation was conducted as a part of a general program on the study of nickel deposition in progress at the Bureau of Standards. It has long been recognized that acidity is an important factor in securing good deposits of nickel but up to very recent times methods for its measurement and control have not been generally known or applied. A study of the regulation of acidity has therefore been made, the results of which have been published in considerable detail[1]. The purpose of the present paper is to explain in

[1] M. R. Thompson "The Acidity of Nickel Depositing Solutions", Trans. Am. Electrochem. Soc. 1922, 41, 233.

simple terms the principles involved in the various methods proposed for measuring acidity and their possible applications to commercial nickel plating and electrotyping. For details the original article should be consulted.

II. GENERAL PRINCIPLES

The fundamental principles of acidity were discussed in a previous paper[2]. This article should be consulted in connec-

[2] W. Blum and M. R. Thompson - "Principles Underlying the Acidity of Nickel Plating Solutions", Monthly Review Am. Electroplaters' Soc. August 1921, 8, No. 8.

tion with the present paper. It may be summarized as follows:

All acids when dissolved in water are decomposed or "dissociated" to a certain extent, with the formation of hydrogen

ions. The extent of the dissociation is a measure of the strength of an acid. Sulphuric acid is strong, i.e. forms a high concentration of hydrogen ions; acetic acid is weak (forms few hydrogen ions), and boric acid is very weak(forms very few hydrogen ions). It is necessary, therefore, to distinquish between the concentration of acid and the concentration of hydrogen ions in any solution. The former is a measure of the amount of acid present, the latter of the degree of acidity. This latter may be expressed in various ways, the simplest being in terms of the pH system. In this system a pH of 3 indicates that the hydrogen ion concentration is 1/1000 normal (i.e. $1/10^3$), and a pH of 4, 1/10,000 normal (or $1/10^4$). The larger the number of the pH, the smaller the acidity, and vice versa. Thus a solution with pH = 5, is only 1/10 as acid as one with pH = 4. For many practical purposes the numbers in the pH system may be considered as arbitrary points on a scale, similar to gage numbers for wire and sheet metal, which also increase as the size decreases.

III. MEASUREMENT OF ACIDITY

It is possible in any solution, such as one used for nickel plating, to determine the total concentration of "free acid" by means of a suitable "titration". It is also possible to measure the degree of acidity by means of indicators. Either method gives information which may be useful, and in certain cases both methods may be applied to advantage. As however the degree of acidity is usually most directly related to the behavior of the solution, its measurement will be described first.

1. Degree of Acidity.

The degree of acidity may be measured "qualitatively" or "quantitatively". In the first method, the purpose is simply to determine whether one solution is more or less acid than some other solution arbitrarily chosen for comparison. In the latter method the extent of the difference in degree of acidity is expressed numerically.

In both cases certain dyes known as "indicators" are employed. For practical purposes an indicator may be defined as a substance whose color changes definitely with a change in the pH or degree of acidity of a solution. All platers are familiar with litmus, usually applied as litmus paper, which has a pink color if a solution is "acid", blue if "alkaline" and purple if "neutral". The terms acid, alkaline and neutral are however relative terms, and for their precise definition accurate measurements may be required. For this purpose a great number of indicators have been developed, each of which has a sensitive color change in some portion of the pH scale.

A. Qualitative Tests.

When litmus paper is introduced into a nickel plating solution, a rough indication is obtained from the color produced, as to whether the solution is acid or alkaline, or more strictly speaking, whether it is more acid or more alkaline than a solution which would produce a purple or neutral tint with litmus. For testing solutions, it is preferable to employ solutions of indicators, as it is difficult to secure test papers of uniform color, or to compare their colors accurately. Storey[1] has described the use of methyl red for this purpose.

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[1] O. W. Storey - A Simple Method for Maintaining the Neutrality of Nickel Plating Solutions - Monthly Review Dec. 1921, 8, No. 12.

In his method, a few drops of the methyl red solution are added to a definite volume (e.g. 5 cc) of the plating solution contained in a small tube, and the color of the solution is noted, and may be compared with the color produced in a sample of any other solution. Such a test indicates whether the solution is more or less acid than has been found desirable in that plant.

It has been found by us that in the pH range in which most nickel solutions give good deposits, another indicator, "bromcresol purple", is somewhat more sensitive and convenient than methyl red. Its solution is applied just like the methyl red above described. The preparation of the indicator solution is described later in this paper.

B. Quantitative Tests.

If a nickel solution is tested with litmus paper and also with congo red paper (the colors of which are the reverse of litmus, i.e. are pink for alkaline and blue for acid), it may be found that the solution is apparently acid toward litmus (turns it pink) and alkaline toward congo red (also turns it pink). By this double test it is possible to define the acidity as within (or outside of) certain approximate limits. Litmus turns pink at about pH=6 and congo red at about pH=4, therefore the above solution would have an acidity within those limits. By testing with both litmus and congo red, the solution may be controlled somewhat more accurately than with litmus alone.

The actual measurement of the pH, or degree of acidity, is similar to the test just described, in that it defines the acidity within certain values, which are fixed by specific

colors of suitable indicators. The standards of comparison may consist either of solutions of known pH independently measured or of tubes containing indicators in such proportions as to produce colors corresponding to definite pH values. The latter, known as the drop ratio method, is most convenient for approximate measurements.

If an excess of acid is added to a solution containing a definite amount of an indicator, all of the indicator will acquire the color corresponding to the acid color of that indicator. If instead an excess of alkali is added to an equal amount of indicator under the same conditions, the alkaline color is produced. If now the acid tube is held in front of the alkaline tube the apparent color observed when light is transmitted through the two tubes will be the same as if the degree of acidity were such that half of the total amount of indicator used was converted to its acid color and half to its alkaline color. The pH corresponding to definite ratios of the acid and alkaline tubes must be determined separately. This has been done for the usual indicators and the data have been published in tabular form as illustrated in Table I. More detailed information regarding indicators and the measurement of pH will be found in a recent book by W. M. Clark[1].

[1] W. M. Clark - "The Determination of Hydrogen Ions", Williams and Wilkins Co., Baltimore, Md.

Table 1.

Constants for Indicator Color Standards

Drop Ratio		pH Number for Each Pair of Tubes	
Alkaline Tube	Acid Tube	Methyl Red	Brom Cresol Purple
1	9	4.05	5.3
1.5(3)	8.5(17)	4.25	5.5
2	8	4.4	5.7
3	7	4.6	5.9
4	6	4.8	6.1
5	5	5.0	6.3
6	4	5.2	6.5
7	3	5.4	6.7
8	2	5.6	6.9
8.5(17)	1.5(3)	5.75	7.0
9	1	5.95	7.2

To apply the drop ratio method, small glass tubes are arranged in pairs in a convenient rack. Each of the tubes should have a scratch mark at a point corresponding to a volume of 5.2 cc (as measured from a burette). To each pair of tubes the same total volume (10 drops) of indicator solution is added, but in different proportions in the front and back tubes of the pair. Thus in the first pair, 1 drop of indicator is placed in the front tube and 9 drops in the rear tube; in the second pair there may be 2 drops in front and 8 in back, and so on. (For practical purposes it is usually found convenient to prepare tubes having ratios of 1.5 to 8.5, at each end of the scale. These are conveniently made up by using 3 and 17 drops of an indicator solution half as strong as that usually employed.) A few cc of water is added to each tube, and to each of the tubes in the front row, a drop of dilute (about 0.05-N) sodium hydroxide, and to each in the back row a drop of dilute (about 0.05-N) hydrochloric acid is added. Water is then added to all the tubes up to the 5.2 cc mark and the contents are mixed. Under these conditions, the colors observed by looking through the two tubes of each pair are the same as would be produced in a tube with 10 drops of indicator in 5.2 cc of solution having the corresponding pH numbers designated in Table I. These color standards may alter and should be freshly prepared at least once a week. The stock indicator solutions are stable.

To test the nickel solution, place 5 cc (after filtering if necessary) in one of the tubes, add 10 drops of the indicator, and mix. When the solution to be tested is colored, as is the nickel solution, it is necessary to place with each pair of color standards a tube containing 5 cc of the nickel solution and 0.2 cc of water. Two tubes of water are placed with the tube of nickel solution containing indicator (only one tube of water would be used with a colorless solution). Comparisons are conveniently made in a small wooden block in which nine vertical holes are drilled nearly to the bottom to accomodate 9 tubes, and three horizontal holes are drilled half way up, from front to back, each intersecting three of the vertical holes. The block should be painted black inside and out. The tubes are placed in the block in the order shown in Table II, and the colors are viewed against diffused daylight (e.g. the sky, or ground glass). The purpose is to select two pairs of standard tubes between which as thus viewed lies the color of the nickel solution. If, e.g. this is about midway between the tubes corresponding to a pH of 5.7 and 5.9, the pH of the solution is designated as 5.8. If it closely matches one pair, the pH is the same as of that pair.

Table II.

Plan Diagram of Comparator Block.

Color Standard Tube (acid)	Water Tube	Color Standard Tube (acid)
Color Standard Tube (alkaline)	Water Tube	Color Standard Tube (alkaline)
5 cc Nickel Solution + 4 drops Water	5 cc Nickel Solution + 10 drops Indicator	5 cc Nickel Solution + 4 drops Water

Either methyl red or brom-cresol purple may be used, but the latter best covers the range of electroplating and electrotyping solutions. A 0.02 per cent solution of methyl red may be made by grinding 0.05 g of the dry indicator with a little 95 per cent ethyl alcohol (or ethyl alcohol denatured with methyl alcohol), dissolving in 150 cc of the alcohol and diluting to 250 cc with distilled water. A 0.04 per cent solution of brom-cresol purple is prepared similarly from 0.1 g of the dry indicator.

The necessary apparatus for the drop ratio method is given in the following list:

2 - Dozen Glass Specimen Tubes (Shell Vials). Medium to thin wall; flat bottom; 12.5 mm (0.5") outside diameter by 75 mm (3") high.

1 - Test Tube Rack, with a double row of at least six holes; to suitably hold tubes of the above size.

1 - Wooden Comparison Block, as per description in text.

4 - 50 cc (2 oz.) Dropping Bottles; rubber bulb type (one for water, the other three for the following solutions).

50 cc (2 oz.) of about 0.04 per cent Alcoholic Brom-Cresol Purple solution.

50 cc (2 oz.) of about 0.05-N-Hydrochloric acid solution.

50 cc (2 oz.) 0.05-N-Sodium Hydroxide solution.

2 - 9 cm (3 1/2") Glass Funnels.

1 - Box Filter Paper, 15 cm diameter.

1 - Filter Stand.

1 - 5 cc Pipette.

1 - 25 cc Burette.

1 - Burette Stand.

2. Titration of Amount of Acid (or Alkali) Present.

Measurement of the pH by means of indicators determines simply the degree of acidity, which has a close relation to the character of the deposit produced. If, however, it is found in any case that the pH differs materially from that considered to be favorable, it is desirable to know how much acid or alkali should be added to restore the desired pH. Such information may be gained by titration of the solution with acid or alkali, using some appropriate indicator. Ordinarily it is assumed (but not always correctly) that in such a titration the actual amount or concentration of free alkali or free acid present in the solution is determined. In the control of nickel solutions, we are not usually concerned with the amount of acid or alkali present in the solution but with the amount of alkali or acid required to "neutralize" the solution, in other words to produce in it some desired pH. The simplest way to determine this is to titrate the solution with alkali or acid with an appropriate indicator (e.g. brom-cresol purple) until the desired neutral color (a deep green with this indicator) is obtained. If as has often been done in commercial plants, the solution is titrated with an indicator such as sodium alizarin sulphonate (the neutral point of which is not the same as the pH desired) the results may be of value but not so directly as with brom-cresol purple. In the former case the solution is considered satisfactory when it has a certain definite "alkalinity"; in the latter it is usually satisfactory when "neutral", i.e. not requiring any acid or alkali.

To titrate a sample of nickel solution, first note carefully whether it is "acid" or "alkaline" to brom-cresol purple by adding 5 to 10 drops of the 0.04 per cent indicator (prepared as previously described) to 50 cc of filtered sample measured into a small flask or beaker. If the color observed is greenish yellow, the solution is "acid" and standard alkali solution will be required for titrating to neutrality. If the color is violet, the solution is "alkaline" and standard acid solution will be required. If the solution shows a deep green color, it is "neutral" to this indicator and no titration is necessary.

Assuming that a given sample is "acid", run in 0.1-N sodium hydroxide from a burette, shaking the flask frequently until a permanent deep green color is produced. Each cc of 0.1-N alkali used in titrating a 50 cc sample corresponds to 0.080 g/L or 0.011 oz/gal of sodium hydroxide; or to 0.120 g/L or 0.0178 fluid oz/gal of aqua ammonia (sp.gr. 0.90). If, in a titration as described above, 50 cc of sample required 5.3 cc of 0.1-N sodium hydroxide to titrate to neutrality, the solution will require for its neutralization:

5.3 x 0.080 = 0.42 g/L sodium hydroxide
or 5.3 x 0.011 = 0.058 oz/gal " "

For 300 gallons, the total requirement would be 300 x 0.058 = 17.4 oz. of sodium hydroxide (stick caustic soda).

The same solution could be neutralized by adding:

5.3 x 0.120 = 0.64 g/L aqua ammonia (sp.gr. 0.90)
or 5.3 x 0.0178 = 0.094 fluid oz/gal " " "

For 300 gallons, the total requirement would be 300 x 0.094 = 28.2 fluid oz. of aqua ammonia.

If another sample of nickel solution proved to be alkaline to the indicator, it should be titrated to the same neutral color of brom-cresol purple, in a similar manner, using standard acid solution. Each cc of 0.1-N sulphuric acid corresponds to 0.105 g/L or 0.0073 fluid oz/gal of commercial sulphuric acid (sp.gr. 1.84; 66°Be). If 50 cc of such a sample required 3.4 cc of 0.1-N sulphuric acid, the solution will require for its neutralization:

3.4 x 0.105 = 0.36 g/L Commercial sulphuric acid (sp.gr. 1.84; 66°Be)
or 3.4 x 0.0073 = 0.025 fluid oz/gal Commercial sulphuric acid (sp.gr. 1.84; 66°Be).

300 gallons would therefore require a total of 300 x 0.025 = 7.5 fluid ounces of sulphuric acid.

Various substances may be used for neutralizing the solutions in the tanks. Nickel carbonate has the advantage that it introduces no other metals but nickel. On the other hand, its composition is somewhat indefinite and it dissolves slowly. ("Plastic" carbonate dissolves more rapidly but is still more indefinite in composition.) If slight additions are only occasionally required, caustic soda may be used in baths containing sodium chloride. In any case, it is preferable to make the additions slowly, and especially if previous experience is lacking to add e.g., only half the amounts calculated from the titration and to then test the pH before adding the remainder. At best, the calculated amounts are only approximate, owing to the possible presence in the tanks of suspended impurities which may partly dissolve in and neutralize the reagent added. After each addition the solution should be well mixed and allowed to settle. Such changes are therefore best made late in the day, or on Saturdays.

A convenient stock of apparatus for applying the titration method should include:

2 - 25 cc Burettes.

1 - Double Burette Stand.

1 - 50 cc Pipette (or a 50 cc graduate can be substituted in most cases).

6 - 100 cc Erlenmeyer Flasks

1 - Liter of 0.1 - N Sulphuric Acid solution.

1 - " " " " Sodium Hydroxide " .

50 cc 0.04% Alcoholic Brom-cresol Purple solution.

1 - 50 cc Dropping Bottle (rubber bulb type preferred; for containing the indicator).

2 - 9 cm. (3 1/2") Glass Funnels.

1 - Filter Stand.

1 - Box 15 cm. diameter Filter Papers.

This list of apparatus duplicates a few pieces that are described under the drop ratio method; when ordering supplies both for that test and for titration work, due allowance should be made for this fact.

IV. CONTROL OF ACIDITY.

Under ideal conditions, with equal anode and cathode efficiencies the pH should remain practically constant, since the removal of solution adhering to the work only results in dilution, which has little effect on pH. Acid or alkali may, however, be introduced into the baths from improper rinsing of the work to be plated. In general, an increase in acidity (decrease in pH) is an indication of insufficient anode corrosion and vice versa. Poor anode corrosion may be remedied by (a) the use of more soluble anodes, (b) cleaning the anodes frequently, (c) using a larger anode area, or (d) increasing the corroding power of the solution.

The pH of some nickel solutions is more affected by a given addition of acid or a given deficiency in anode corrosion than is that of others. Those solutions which are least affected are said to be "well buffered". In general, such solutions contain weak acids or their salts. Thus boric acid, used very generally in nickel baths, owes its beneficial effect principally to its buffer action and consequent regulation of acidity.

Solutions containing hydrofluoric acid (or fluorides) together with boric acid are still better buffered. A well buffered solution is usually desirable. Whether the use of any given substance to increase buffer action is advantageous or not will depend upon other effects that it may have upon the deposition.

V. EFFECTS OF ACIDITY.

Acidity of nickel solutions is only one of the factors which determine the character of the deposits, and it must not be supposed that its control will of itself insure good deposition. If controlled, however, the possibility of poor deposits occurring is decreased and their cause is more readily determined. The following conclusions, drawn from experiments conducted with various types of solutions at the Bureau of Standards, are tentative, and subject to modification when more complete information is available regarding the simultaneous effect of acidity and other factors, such as, e.g. the presence of iron in the solutions.

1. In general, good nickel deposits are produced when the cathode efficiency is high, i.e. when there is little hydrogen evolved (so-called "gassing") at the cathode.

2. Within the usual working range, the cathode current efficiency increases as the pH increases, up to about pH = 6.

3. For a constant pH, the cathode efficiency increases as the current density is raised, within certain limits, which latter are dependent in part on the type of solution used.

4. Better deposits may be secured in a solution of low pH (high acidity) at a relatively high than at a low current density.

5. Where it is necessary to use a low current density, e.g. on irregularly shaped articles, the pH should be comparatively high (low acidity).

6. Deposits made in a solution of low pH (high acidity) are likely to be finer grained, brighter and harder, but more brittle than those from solutions with high pH.

7. With any pH up to 4, the deposits are bright but very likely to show excessive cracking and pitting. A pH of 4 is, therefore, the lower limit of good deposition.

8. With any pH above 6.5 the deposits are dark, and cracking and curling are likely to occur. In still solutions it is difficult to obtain good deposits above pH = 6.5. In agitated solutions, as in electrotyping, good deposits may be made up to nearly pH = 7.

The above conclusions were in general confirmed by observations made in a number of commercial plants. It was found that practically all satisfactory nickel plating is conducted in solutions with a pH between 5.4 and 6.3. The average of the larger plants (in which the solutions were controlled by other analyses) was found to be about 5.7. This value is suggested for trial to those who desire to measure and control acidity in nickel plating. In agitated electrotyping solutions, the average is about 6.3.