Characterization of Bright/Semi-bright Nickel Electrolytes & Corrosion Properties of the Corresponding Nickel Deposits

By W. Dahms, R. Schumacher & J.M. McCaskie

The capability of cyclic voltammetry for the characterization of bright and semi-bright nickel electrolytes is reported. Evaluation was made of the effect of various organic additives on the features of the resulting cyclic voltammograms. A method for quantifying of these additives is outlined. In addition, cyclic voltammograms are evaluated in terms of the corrosion performance of the nickel deposits. These data were compared with STEP test data.

Electroplating with nickel plays a major role in finishing parts for the automobile and bicycle industries. Surface finishing of plumbing fixtures is another important industrial application of nickel electroplating. Here, too, both plastic and metallic base materials are used. These industries require not only a particularly decorative finish, but also that the formed deposits be resistant to corrosion. To attain these quality features, manufactures use electrolyte combinations consisting of high-quality, sulfur-free, semi-bright electrolytes and leveling bright nickel electrolytes.

Production of nickel layers with consistently superior quality characteristics requires simple but precise process control and analytical methods. Aside from the inorganic components of the electrolytes (nickel sulfate, nickel chlorides, boric acid), the organic additives in the electrolytes are of critical importance for the properties of the nickel deposits produced. As is well known, these additives are added to the electrolytes at low concentrations. Their wet chemical determination, though, is difficult. Both polarographic and titrimetric methods, such as iodimetry, for example, have proved good for determination of pyridine derivatives, saccharin, or unsaturated organic compounds. Recently, chromatographic methods have been employed to determine the concentrations of the active ingredients. In this connection, High Performance Liquid Chromatography (HPLC) a technique derived from methods of analysis of the liquid volume phase is used. Although useful for quantification, this technique gives information about the electrochemical activity of the organic electrolyte additives.[1,2]

An analytical procedure based on the electrochemical activity of organic additives was developed, using cyclic voltammetry.[3] This methodology, also called CVS for brevity, has become widely used in the last decade for determining organic additives in acid copper electrolytes.[4] In this procedure, the amount of electrical charge consumed or generated in the deposition and dissolution of the copper layer is evaluated to determine the active substances in the electrolyte. It has not previously been possible to transfer this elegant research method to control of nickel electrolytes.[5] In the following, therefore, we first present the initial results of CVS studies developed to characterize and quantify organic additives in nickel electrolytes.

Experimental Procedure

The conventional measurement vessel holds 50 mL of electrolyte and is equipped with a thermostatic section. This setup allows continuous temperature adjustment to working conditions of 55 °C. The working electrode in the three-electrode system was a rotating platinum disk, 3 mm in diameter. The counter-electrode was a platinum rod (dia.: 1 mm). A silver/silver chloride electrode was used as the reference.

A potentiostat was used as the voltammetric device and a voltammetric scanner was used as the potential source. The upper and lower potential scan limits of +1.3 V and -1.1 V were determined in preliminary experiments. The scan rate was 100 mV/sec. The voltammograms were recorded with the disk electrode rotating at 2000 rpm. Variation of the speed of rotation between 1000 and 3000 rpm has only a slight effect on the peak areas and, consequently, on the charge quantity, Q, involved in the stripping process. A Spectra Physics SP 4200 integrator was used to determine Q. The

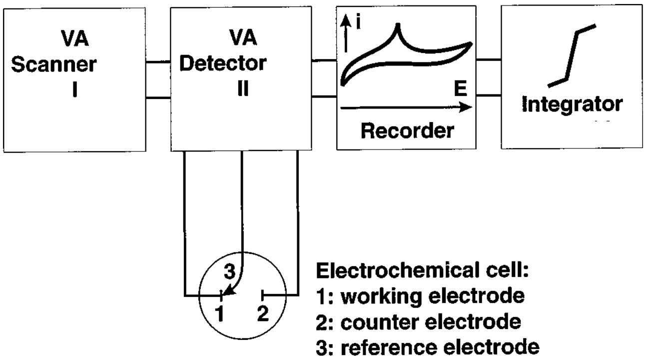

Fig. 1—Set-up for recording cyclic voltammograms.

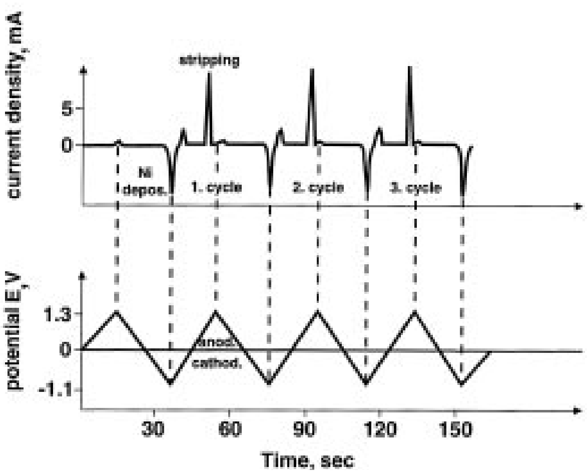

Fig. 2—Measurement principle for recording cyclic voltammograms.

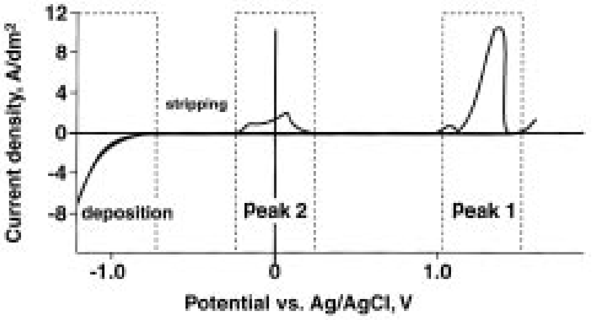

Fig. 3—Cyclic voltammogram for a Watts nickel electrolyte.

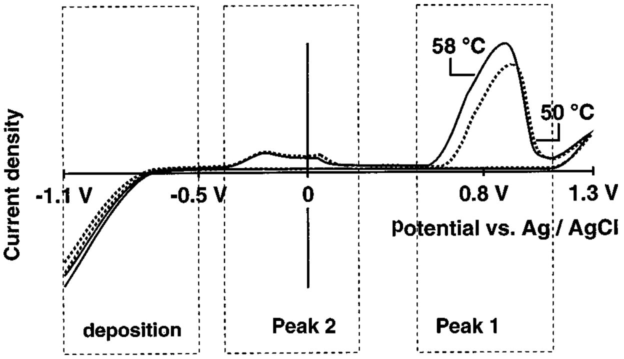

Fig. 4—Cyclic voltammogram of a nickel electrolyte at different electrolyte temperatures.

detector amplification was 20 mA/V, corresponding to an amplification at the recorder of 0.4 mA/V. Figure 1 shows the measuring system.

Figure 2 shows an overview of the measuring principle for recording cyclic voltammograms. It involves variation of the electrode potential with a specified constant scan rate within a specified potential window, in this case, between -1.1 and +1.3 volts. As Fig. 2 shows, the potential scan is a sawtooth wave (lower part of the figure). The resulting current-voltage curve for nickel electrolyte is shown in the upper part of the figure.

Process Electrolyte

Tables 1 and 2 list the composition of a Watts nickel electrolyte, with typical concentration ranges for the inorganic and organic components. Only the leveler additive and wetting agent are used in semi-bright electrolytes.

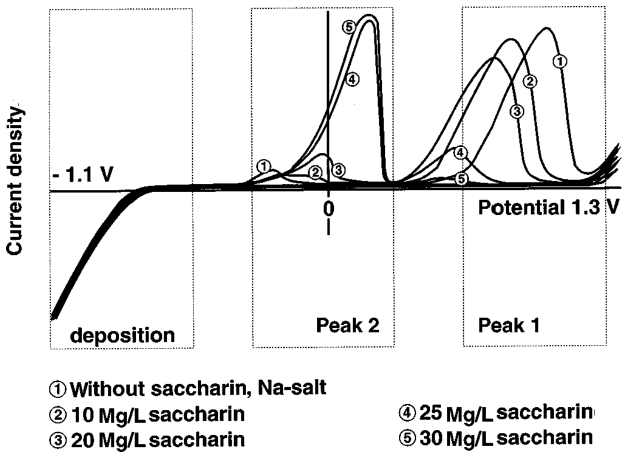

Fig. 5—Alteration of the cyclic voltammogram by saccharin.

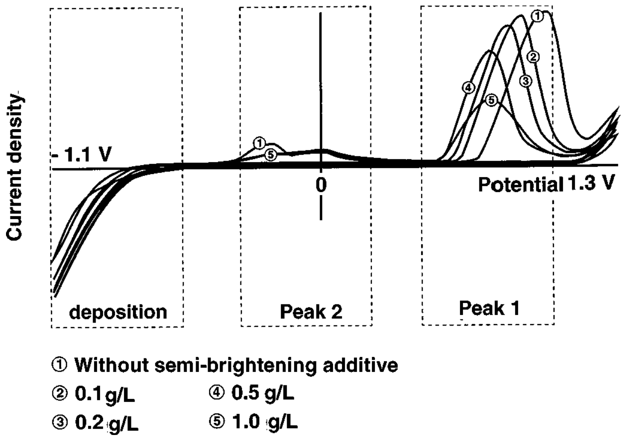

Fig. 6—Alteration of the cyclic voltammogram by a semi-bright additive.

Cyclic voltammogram in the potential range for electrochemical deposition & dissolution of nickel

Figures 3 and 4 show typical recordings of cyclic voltammograms obtained by using various process electrolyte compositions. The figures refer to three processes: Nickel deposition occurs below -0.5 volt, while two distinctly different potential ranges were identified for potential-controlled nickel dissolution (stripping). It is interesting to note that the anodic charge below the stripping peaks is influenced both by the temperature of the process electrolyte and by its composition.[6] These findings are described in the following sections. As seen in Figs. 3 and 4, the following anodic and cathodic processes are of interest: Deposition range from -1.1 to -0.5 V; stripping range 2, from -0.4 to +0.2 V; stripping range 1, from +0.5 to +1.1 V. The recording in Fig. 3 was obtained using a nickel electrolyte free of additives.

Effect of temperature

Figure 4 shows a typical voltammogram recorded, using a Watts nickel electrolyte (Composition: 71 g/L Ni^{+2}; 14.3 g/L Cl^-; 38.4 g/L H_3BO_3), at different temperatures. The electrolyte was purified with activated charcoal. The diagram shows that the charge quantities under the stripping peaks increase with increase of the temperature of the process electrolyte. For explanation, it is assumed that the nickel deposition is an exothermic process with a correspondingly high activation energy. The electrolyte temperature, therefore, becomes a critical experimental parameter. It was held constant at 55 +0.5 °C by means of a suitable thermostat system. This also corresponds to the electrolyte temperature used in practice.

Effect of inorganic constituents of the electrolyte

The effect of the inorganic constituents on the magnitude of the stripping peaks is summarized as follows: Changing the concentration of nickel ions in the range from 80 to 100 g/L causes a negligible change in the magnitude of Peak 2. Below 50 g/L Ni^{+2}, however, a decrease is observed. Similarly, no change in the magnitude of Stripping Peak 2 was observed for boric acid concentration in the range from 30 to 50 g/L. The result was different for variation of the chloride content. Increasing the chloride concentration from, for example, 9 to 15 g/L causes the area nearly to double. All further studies were done, therefore, with constant chloride concentration (12 g/L). In a chloride-free electrolyte, electrochemically deposited nickel is not dissolved in the range of Stripping Peaks 1 and 2.

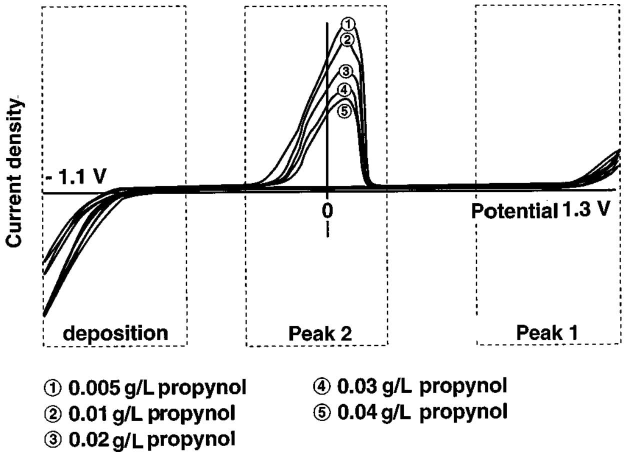

Fig. 7—Alteration of the cyclic voltammogram by propynol.

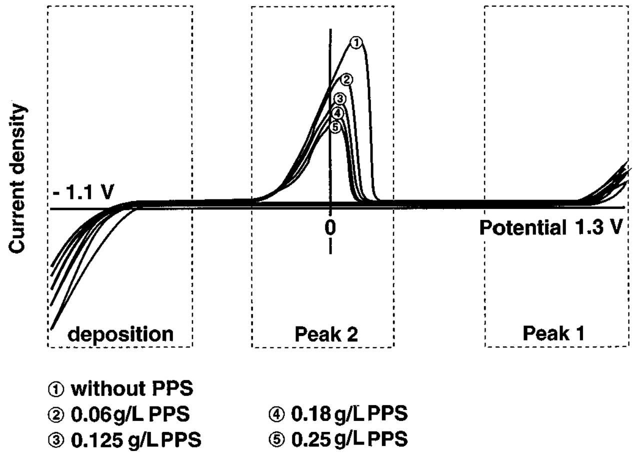

Fig. 8—Alteration of the cyclic voltammogram by pyridinium-N-propylsulfobetaine (PPS).

Effect of organic additives

It can be seen from Figs. 5 to 9 that anodic nickel dissolution occurs in the potential range of -0.4 to 1.2 V. Depending on the electrolyte composition, dissolution occurs either consecutively in the potential ranges 2 and 1 (*cf.* Figs. 3-6 and 9) or dominantly in one of the potential ranges (compare Figs. 5, 6, and 9 with Figs. 5, 7, and 8). The observation that nickel dissolution occurs within two separate potential regions contradicts observations collected using acid copper electrolytes. The anodic dissolution of copper films deposited under these conditions occurs only in the potential range of 0 to -300 mV. The conjecture that one of the two stripping peaks is the result of a contaminant in the electrolyte, introduced by the inorganic electrolyte components used, proves untenable. It could be shown that neither purification of the electrolyte with activated charcoal, nor use of high-purity nickel salts or boric acid (99.999%) made any change in the anodic current/potential window.

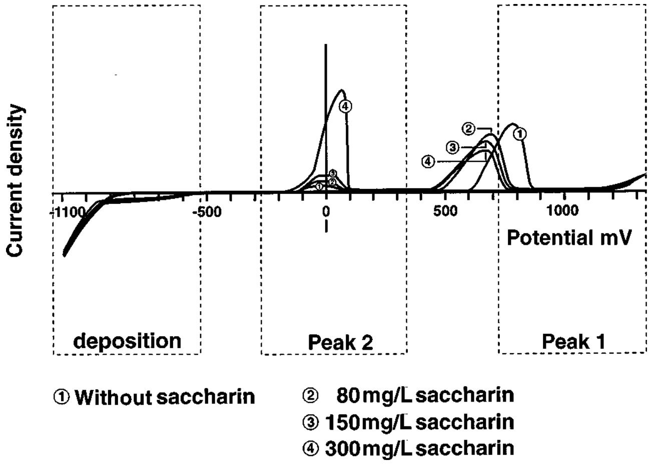

Fig. 9—Alteration of the cyclic voltammogram curve by saccharin in semi-bright nickel electrolyte.

We consider it highly probable that the anodic processes observed by varying the electrolyte composition result from formation of different nickel crystal structures during deposition. This situation corresponds to electroless nickel films. The nickel phase dissolved in potential range 2 represents finely crystalline material, while that dissolved in potential range 1 is coarsely crystalline columnar material. Both the coarsely crystalline and the finely crystalline phase of the material can be made dominant by adding suitable organic electrolyte additives. Figure 10 shows microsections of the material structures obtained from electrochemically generated duplex nickel layers.

A summary of the results derived from the CVS studies of the organic additives used in this study, and their effects on the film-forming process, can be classified as follows:

- Substances such as saccharin, aromatic sulfonic acid derivatives, and the brightening agents shift the stripping potential (Peak 1) to the vicinity of zero potential (Peak 2). As a consequence, Peak 1 vanishes completely (see Table 2).
- Substances such as typical levelers like hydroxyalkynes and pyridinium compounds only slightly affect the stripping potential. As their concentration increases, however, they reduce the anodic charge transfer.
- Substances such as typical brightener additives that both shift the stripping potential and reduce the anodic charge below the stripping peak.
- Substances such as wetting agents having practically no effect on the voltammogram.

CVS Analysis of Brightening Agents and Levelers

Methods for Brightening Agents

The effect of saccharin, a brightening agent often used in bright nickel electrolytes, can be seen from the cyclic voltammogram of Fig. 5. In that study, up to 30 g/L of saccharin were added to the electrolyte. The individual curves show clearly that the charge quantity under the Stripping Peak 1 decreases with increasing saccharin concentration, while Peak 2 grows continuously. The maximum or minimum value is reached at about 30 mg/L.

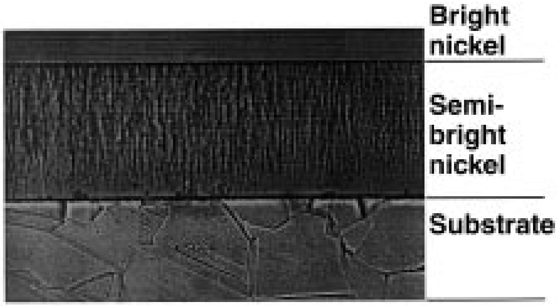

Fig. 10—Cross section of crystallographic structure of a duplex nickel layer.

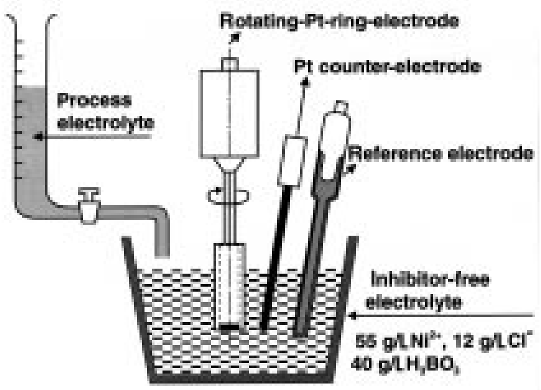

Fig. 11—System for determining brightener content by dilution titration.

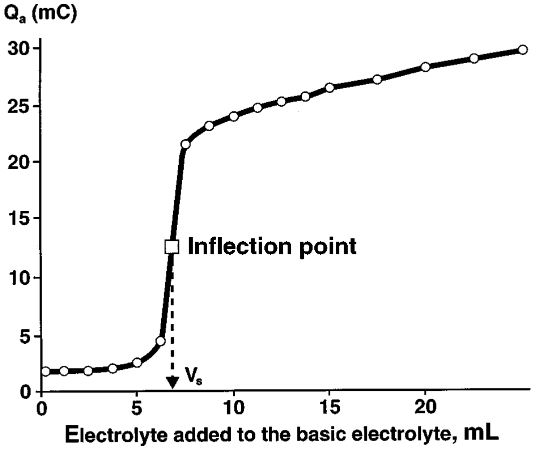

Fig. 12—Evaluation of the dilution titration for determining brightener content.

The methodology for determining the brightening agent concentration by CVS technique was derived on the basis of the observations presented in Fig. 5. The method uses the principle of dilution titration in such a manner that specified volumes of a production electrolyte are added to the additive-free nickel electrolyte. The measured quantity is the resulting depression of the charge Q_a found for the anodic nickel dissolution in potential range 1. Figure 11 shows the apparatus developed for this measurement. The plot of Q_a vs. V, in Fig. 12, shows a titration type of curve for an electrolyte having the standard composition. V is the volume of working electrolyte added to the base electrolyte in the course of the measurement. Q_a is the anodic charge transfer corresponding to nickel dissolution in potential range 1. Figure 13 shows the different curves for the plot of Q_a/Q vs. V, using a standard and a production electrolyte with $c_s < c_x$ (c_s and c_x are the brightening agent concentrations in mL/L, in the standard and in the production electrolyte being analyzed). The decrease in charge in potential region 1 is described by the quantity Q_a/Q, which is normalized to 100 percent. The figure shows a shift in electrolyte volume V that must be titrated to reach the inflection point. In the case shown here, $V_s > V_x$. V_s was determined using the standard electrolyte, and V_x by using the process electrolyte. Studies with nickel electrolytes mixed with different concentrations of brightening agents led to the following result: The content of brightening agent, c_x, in any production electrolyte, can be determined from the ratio V_s/V_x, by multiplying it by c_s, the brightening agent content under standard conditions:

$$C_x = C_s V_s / V_x$$

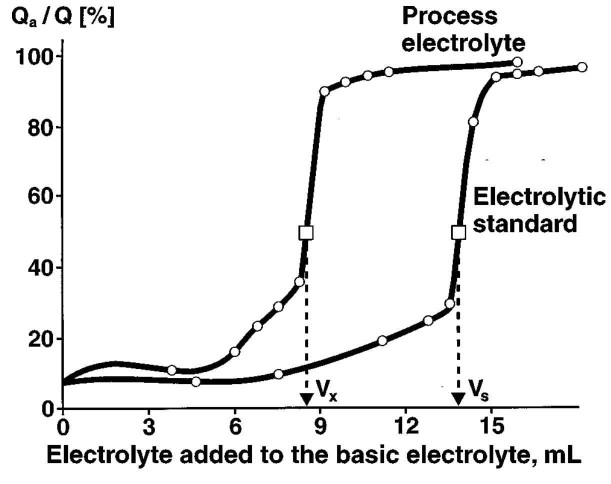

Fig. 13—Evaluation of the dilution titration for determining brightener content in process electrolytes.

Through studies on electrolyte systems of known concentration, it could be shown that this linear relation gives deviations of recovery < 10 percent in the concentration range of 1 to 30 g/L of brightening agent.

Figure 14 shows the concentration profile of the brightening agent, saccharin, as a function of the production life of a nickel bath. The production life is equivalent to the amount of charge, per volume of electrolyte, summed over the individual production cycles. The process quantity of amp-hr per liter of electrolyte (A-hr/L) is common in electroplating practice. The figure illustrates the concentration curve determined by HPLC and CVS in the range up to 300 A-hr/L. The deviations from the concentration curve shown are considered to be associated with the fundamentals of the applied measuring method. It is probable that the use of the CVS technique corresponds to the sum of all electrochemically active additives, including the degradation products, that accumulate in the electrolyte during electroplating. The HPLC technique shows only information about individual components of the electrolytic volume phase.

Method for Levelers

High-capacity electrolytes contain levelers, such as hydroxyalkynols and/or pyridine derivatives. These substances have only slight effect on the stripping potential, but as their concentrations increase, they reduce the charge

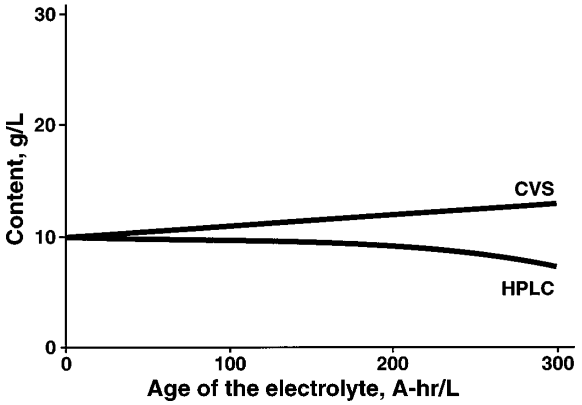

Fig. 14—Plot of brightener content as a function of bath age. Values were determined by CVS technique or HPLC.

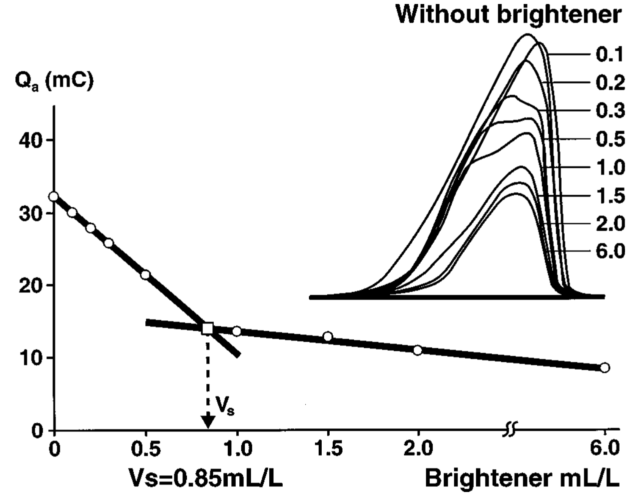

Fig. 15—Calibration curve for determination of brightener content in the presence of carriers.

transfer required for anodic dissolution. That can be seen in Fig. 7, using propynol addition in the presence of brightening agents as an example. Figure 8 shows another example. Here, again, increasing concentrations of leveler, in this case pyridinium-N-propylsulfobetaine (PPS), reduces the charge under Peak 2. As is shown in the following, this effect can be used to estimate the leveler content in the electrolyte.

Estimation of the leveler content

If electrolytes having a fixed brightening agent content are continuously enriched with a commercial brightener additive, the charge quantity represented by Peak 2 decreases. This effect is produced primarily by the levelers always present in the usual commercial brightening additives. Experiments show that beyond a certain minimum concentration, even slight decreases of the charges can be recorded. The right side of Fig. 15 shows the curve for Peak 2 with continuous increase of the brightening additive. If the corresponding charge vs. the brightening additive is plotted, two straight lines with different slopes are obtained. Projection of the intersection onto the concentration axis* gives V_s, thereby describing the standard situation.

Figure 16 shows measurement of a production electrolyte with unknown leveler content. Projection of the point of intersection onto the concentration axis gives a distinctly smaller value for V_x. Then the deviation from the desired value, V_{feed}, can be estimated from

$$V_{feed} = V_s - V_x$$

Experience shows that the actual concentration determined, V_x, is always below V_s. The applicability of this method assumes, though, that the brightening agent concentrations are similar in the unknown sample and in the standard electrolyte. The brightening agent content, therefore, is determined first and corrected to the desired value if necessary.

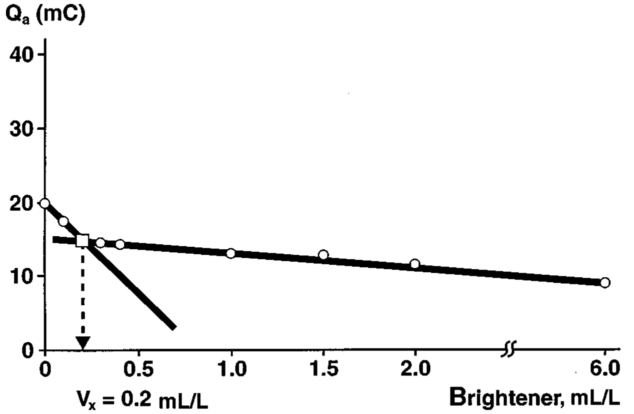

Fig. 16—Graphic evaluation to determine brightener content of a nickel process electrolyte.

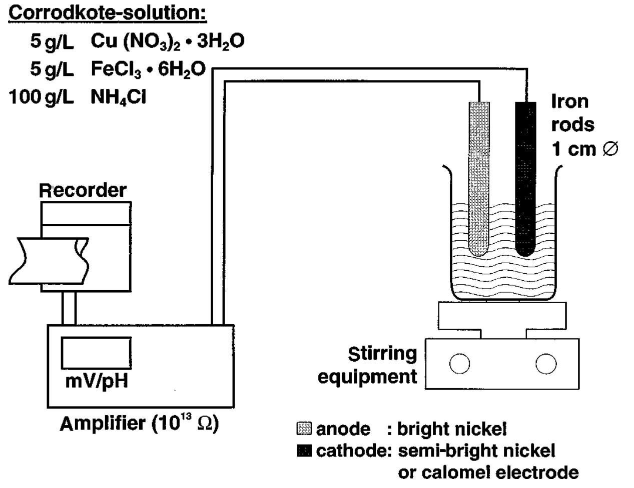

Fig. 17—Experimental set-up for measuring corrosion potential.

Investigations of the corrosion behavior of nickel films deposited from semi-bright nickel electrolytes

Duplex nickel layers are used in practice to improve corrosion protection. In this process, a semi-bright nickel layer with a more passive potential is deposited under the decorative bright nickel layer. The two nickel layers are also clearly distinguished from each other by different crystal structures (see Figure 10). Semi-bright nickel layers usually have a columnar structure, while bright nickel practically always grows with a laminar structure. It is well known that the potentials of these nickel layers, deposited from different electrolyte systems, also differ. The potential difference is particularly high if incorporation of foreign components, such as sulfur, is avoided in the semi-bright electrolytes. It is known from studies using the STEP test that this potential difference is on the order of more than 100 mV. As a rule, the values are more positive for semi-bright nickel layers in contact with standard electrolytes than for bright layers. This

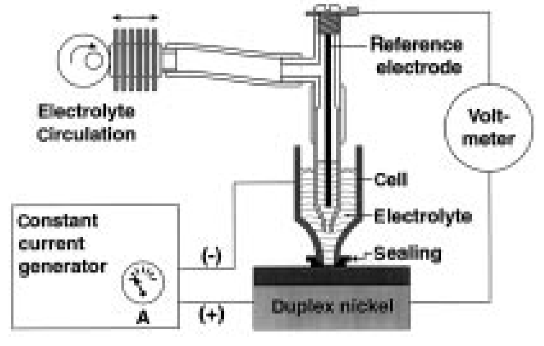

Fig. 18—Experimental set-up for performing the STEP test.

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* Similar relations also occur with surfactants, among other things. This method is used with surfactants to determine the critical micelle concentration (CMC).

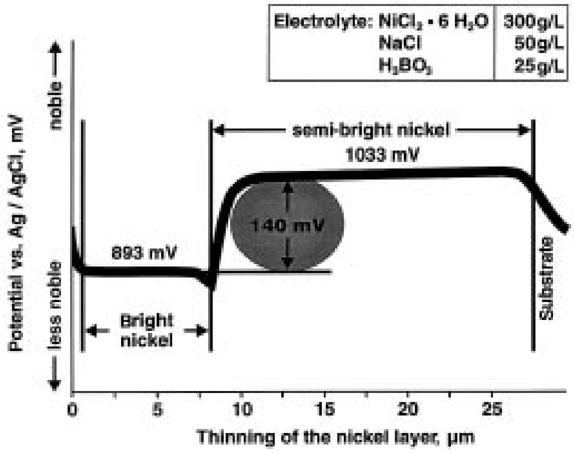

Fig. 19—Potential curve during stripping of a duplex nickel layer.

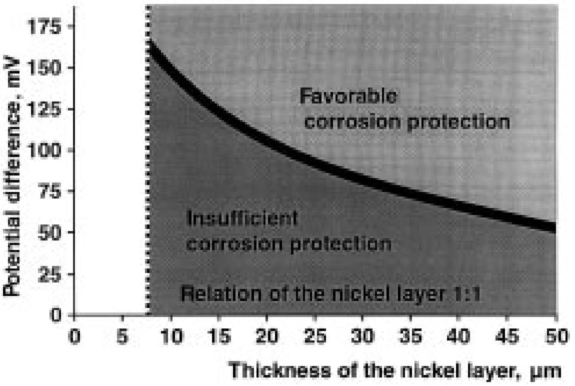

Fig. 20—Relation between corrosion protection and potential difference for a duplex nickel layer.

observation agrees with studies of the corrosion potential.* Here, too, more positive potential values are recorded using semi-bright nickel electrolytes.

Measuring Methodology for Corrosion Characteristics

CASS and Corrodkote test

The process reliability and the process stability of semi-bright nickel electrolytes were inspected on appropriate nickel layers. Either short corrosion tests, such as the well-known CASS or Corrodkote tests, were performed on finished parts, or the corrosion potential of the plated nickel layer was measured in a Corrodkote solution. These examinations were performed on nickel foils or on test rods coated with a 20 to 30 mm thick nickel layer. Figure 17 shows the measuring set-up. A calomel electrode, or a bright nickel foil, or a test rod coated in a bright nickel electrolyte, can be used as the counter-electrode. The potential difference measured is correspondingly different. A potential of -25 to -40 mV is determined with respect to the saturated calomel reference electrode by using a properly working semi-bright nickel electrolyte. Potential differences of 60 to 90 mV are measured vs. a bright nickel layer.

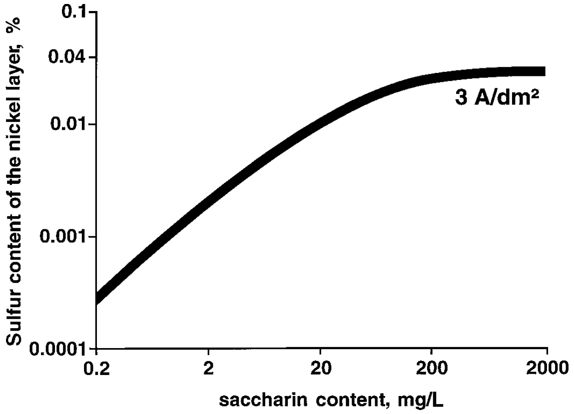

Fig. 21—Increase of sulfur contamination for a nickel layer with increasing saccharin content in the electrolyte.

STEP Test

The STEP (Simultaneous Thickness and Electrochemical Potential) test is based on the anodic stripping of nickel layers deposited on a finished part with 25 mA. Figure 18 shows a suitable test sample. In this method, the nickel layer is stripped galvanostatically and the potential required for stripping is determined. The electrolyte is a conductive salt solution, usually a standardized nickel electrolyte, such as shown in Fig. 19.

If the potential is plotted against the thickness of the stripped layer, a curve such as shown in Fig. 19 results. The chromium layer is stripped first, then the bright nickel layer, and finally the semi-bright nickel deposit. The potential step between bright and semi-bright nickel is measured. In the ideal case, it should be about 140 mV. The dependence of the potential step on the layer thickness and the ratio of the thicknesses of the semi-bright and bright nickel layers is known. The example in Fig. 20 shows the situation for a layer thickness ratio of 1:1. This test allows evaluation of the process electrolytes, with the disadvantage that any irregularities in the electroplating process are recognized only after parts are plated.

Cyclic Voltammetry

Figure 6 shows the cyclic voltammogram, using a semi-bright nickel electrolyte. The anodic stripping of the deposited nickel film occurs in the potential range from 0.5 to 1.1 V. It agrees with the observation made using an additive-free nickel electrolyte (see Fig. 3). When a semi-bright additive is used, the peak maximum shifts only slightly toward less passive values, demonstrating that this effect is not significant enough to be used for process control. On the other hand, a pronounced effect is observed for the intensity of the stripping peak. It decreases as the addition increases. This observation indicates that the CVS technique can be applied for characterizing semi-bright nickel electrolytes similar to acid copper electrolytes.

For one thing, the semi-brightener additive can be determined, like a leveler in bright nickel electrolytes. Also, the position of Stripping Peak 1 makes it possible to estimate the corrosion potential of the nickel layer and the potential difference in the STEP test. To test this prediction, we deliberately contaminated a semi-bright electrolyte with saccharin, so that sulfur was incorporated in the nickel deposit. Figure 21 shows the proportion incorporated. As a consequence, the potential difference observed in the STEP test decreases, resulting in insufficient corrosion protection (see Figs. 20, 22). As the nickel deposit becomes less passive, the corrosion protection also diminishes. Corrosion protection for semi-bright nickel deposits falls below an acceptable limit if the sulfur content exceeds 0.002 percent.

• Also called the resting potential.

Table 1
Composition of a Watts Nickel Electrolyte

Nickel ions	55-85 g/L
Boric acid	35-45 g/L
Chloride ions	10-20 or 35-50 g/L
Temperature	50-60 °C
pH	4-5
Brightener*	3-20 g/L
Mixture brightener and leveler*	0.5-2 g/L
Wetting agent*	1-4 g/L

* Commercial product

Table 2

Carrier	**Leveler**
Chemical classification:	Chemical classification:
Sulfonic acids or sulfonamides, both with aromatic rings	Hydroxyalkynes, pyridinium compounds
Brightener Additive	**Wetting Agent**
Chemical classification:	Chemical classification:
Alkylsulfonic acids	Alkyl sulfates

The relation found experimentally between the position of Stripping Peak 1 and the potential difference in the STEP test is shown in Fig. 23. Accordingly, it appears possible to check the semi-bright electrolyte using the CVS technique, in the sense of quality monitoring during production.

Findings on CVS Determination of Corrosion Performance

The decrease in the corrosion protection of a semi-bright deposit as the sulfur content increases can also be shown with cyclic voltammograms. Incorporation of sulfur results in reduction of the charge required for anodic stripping and in a shift of the peak maximum of Peak 1. It disappears completely with very high sulfur content. At the same time, the intensity of the peak in potential range 2 increases. Both observations can be used for evaluation of the semi-bright electrolyte. The shift of Peak 1 is also reflected in the results obtained using the STEP test. It is known that the potential difference that occurs between semi-bright and bright nickel layers decreases with increasing sulfur content. If nickel dissolution occurs even in potential range 2, the electrolyte is contaminated with sulfur-containing compounds, and the nickel layer generated will be susceptible to corrosion.

In practice, evaluation of the corrosion behavior by cyclic voltammetry can be performed simply and early enough that the production process can be adjusted before parts are produced with inadequate quality.

Conclusions

Both determination of the brightener content in bright nickel electrolytes and determination of the leveler constituents in bright and semi-bright electrolytes, and evaluation of the corrosion behavior to be expected make the methodology described here, based on cyclic voltammetry, an important instrument for quality assurance.

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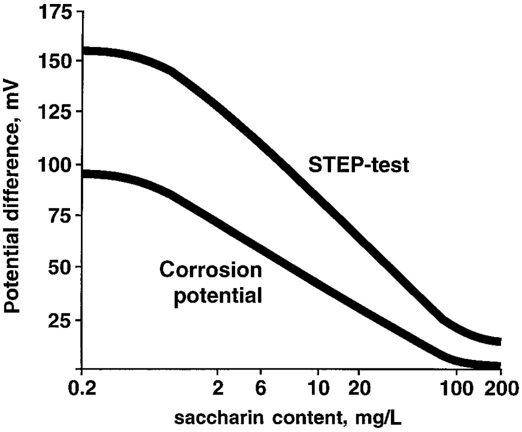

Fig. 22—Decrease of potential difference in the duplex nickel system with increasing sulfur contamination.

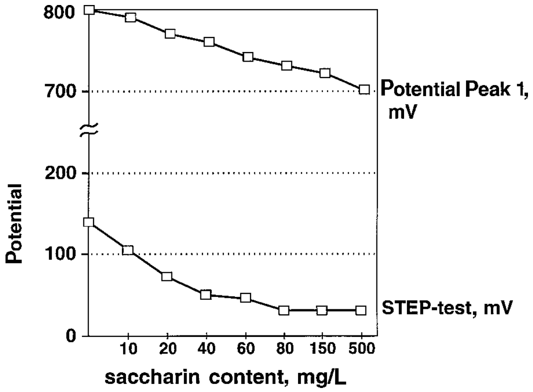

Fig. 23—Effect of sulfur contamination on the absolute potential position of Stripping Peak 1 and the potential difference obtained in the STEP test. Sulfur content of the deposit was varied by increasing the saccharin content of the electrolyte.

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