Jan. 8, 1946. H. E. TSCHOP 2,392,708

METHOD OF MAKING SULPHUR-CONTAINING NICKEL ANODES ELECTROLYTICALLY

Filed Aug. 9, 1941

Fig. 1.

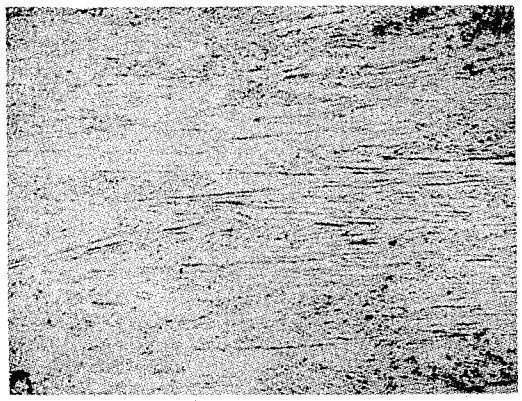
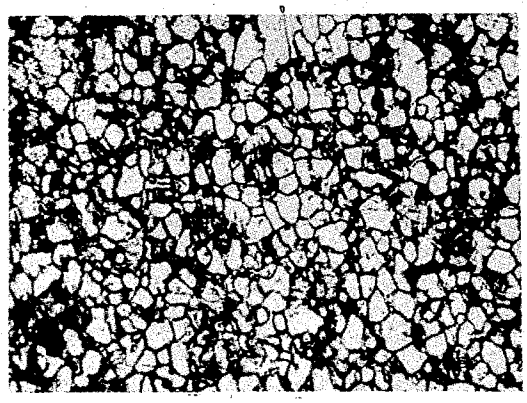


Fig. 2.



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METHOD OF MAKING SULPHUR-CONTAINING NICKEL ANODES ELECTROLYTICALLY

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8 Claims. (Cl. 204—292)

The present invention relates to nickel plating anodes and, more particularly, to electrodeposited nickel plating anodes containing sulphur and a process therefor.

The development of the nickel plating industry has been accompanied by careful consideration of the effect of the composition of the nickel anode upon the plating produced. The earliest nickel anodes contained appreciable amounts of iron and in the earliest days of nickel plating many platers held that the presence of cobalt was advantageous. In the last 25 or 30 years it has been found that nickel anodes containing small amounts of critical elements provided a more satisfactory anode from an operating standpoint than the anodes of the earlier days of the industry. While Spencer has stated:

"It may be observed that the general tendency is toward the development and use of an anode of the highest possible purity containing the lowest possible amounts of carbon, oxygen, iron, silicon, and other contaminating elements. * * *

* * * * * * *

"From what has been said in the preceding pages, it appears that a perfect anode would be one which is chemically pure nickel of uniform crystal size with a high solution potential. But absolutely pure nickel is very difficult to dissolve, so other elements must be present to increase its solubility. Such elements should form solid solutions with nickel and be soluble in a commercial plating solution. * * * It might be said that neither oxygen nor carbon should be present in the anode in greater amounts than can be dissolved and retained in solution by the nickel. In other words, the metal should be clean when etched and examined under the microscope, or, if it is not absolutely clean, the insolubles should be present in a few large, disconnected particles." [The Metal Industry (London) January 22, 1937, p. 142, column 1, lines 10–14 from the bottom; p. 144, column 1, line 7 from the bottom to column 2, line 14] the art has found that anodes containing critical amounts of some or all of these elements are far superior from an operating standpoint to anodes devoid of or containing as little as possible, of these so-called contaminating elements. For example, one of the gravest problems confronting the manufacturer of nickel anodes is the passivity which nickel anodes of high purity develop. Several years ago it was proposed to incorporate in nickel anodes a critical amount of sulphur or a critical amount of oxygen or both in order to provide smooth corrosion and to eliminate passivity. Such anodes have been described and have been provided for the art (Geiger U. S. Patents Nos. 1,941,256 and 1,941,257). However, such anodes in the past have only been produced by melting electrolytic nickel and incorporating the necessary amount of sulphur in ways well known to those skilled in the art. It will be appreciated that the production of electrolytic nickel containing the necessary amount of sulphur would, from an economic standpoint, be a considerable advance in the progress of the art. However, so far as I am aware, no one has proposed or disclosed a process whereby massive deposits of nickel may be obtained electrolytically which contain sulphur in a form providing the corrosion characteristics of sulphur when incorporated during melting and suitable for use as anodes in the electrodeposition of nickel plating for protective and/or decorative purposes.

While it is a fact that thin films of nickel containing extremely small amounts of sulphur have been deposited electrolytically on various base metals for decorative or protective purposes, the problem of electrodepositing massive nickel containing sulphur and suitable for use as anodes in electroplating, has not been solved heretofore. Those skilled in the art will readily appreciate that many factors affect the production of massive deposits of nickel electrolytically which do not arise in the deposition of thin films of nickel.

It is customary in electroplating base metals with nickel for protective and/or decorative purposes to provide the base metal with a very thin film of nickel which in most instances has a thickness of about 0.0001 inch and rarely reaches a thickness of 0.001 inch. In contrast to these very thin films of nickel, anodes for use in the electrodeposition of these thin films of nickel for protective, and/or decorative purposes generally have a thickness of at least about ½ inch and in many instances a thickness of the order of an inch. Furthermore, in the usual electroplating of thin films for protective and decorative purposes the thin film of nickel is supported by the

base metal and consequently the physical characteristics of the film of nickel do not play such an important part. Nickel anodes, on the other hand, must have sufficient strength to support their own weight and must withstand the usual stresses encountered in shipping and in handling the anodes in and out of the electroplating bath. Nickel anodes therefore of themselves must not be brittle to the degree that the anodes would shatter and become useless during the usual vicissitudes of comercial handling. Furthermore, the problems of depositing thick coatings of nickel are recognized and the experts in the art readily understand and agree that beyond a certain thickness many problems arise which have not been solved. (Kugel U. S. Patent No. 665,-915.)

The characteristics of a nickel anode which are of primary importance to the electroplater but do not enter into an evaluation of nickel electrodeposits for decorative and/or protective purposes are the activity of the anode at high pH, the character of the corrosion, the amount of sludge, the character of the sludge and the tendency of the sludge from some anodes to become detached from the corroding anode in small pieces which float or migrate to the work being plated. It will be readily appreciated that the producer of articles electroplated with nickel for protective or decorative purposes usually is not interested in the foregoing characteristics of the protective or decorative plating. Applicant is only aware of one article in the technical literature which discusses the anodic properties of a nickel electro-deposit comparable to the conventional decorative or protective film of electroplated nickel. In an article published in Mitteilungen des Forschungsinstituts and Probieramt fur Edelmetalle for July, 1936, E. Raub discusses the use of insoluble anodes such as lead and rustproof steel by German electroplaters. The following quotation is from a translation of that article:

"More suitable than the use of insoluble anodes is the following process which also is the basis of a proposal of the Langbein-Pfanhauser Werke of Leipzig. Metallic nickel is made electrolytically from nickel salts, which in general are not so difficult to procure as metallic nickel, which then is used as anode in the galvanic nickel bath. The process is of course inconvenient and makes nickel plating expensive but nevertheless in most cases is more to be recommended than the use of insoluble anodes."

Thus it is manifest that this authority clearly considers that electrolytic nickel is only slightly better than insoluble anodes in a process for electroplating protective or decorative films of nickel. A mere recitation of these characteristics of a nickel anode impresses the fact that the mere deposition of nickel electrolytically as a thin film for decorative or protective purposes does not provide the art with the answer to these questions: Will electrolytically deposited nickel-containing sulphur be active at high pH [pH 4.0(Q)]? Will such nickel corrode smoothly? Will the amount of sludge be excessive? Will the sludge adhere to the anode and only break away therefrom in chunks of such size as to sink to the bottom of the tank? It is equally manifest that other questions of similar scope still remain unanswered after the unpremeditated deposition of sulphur in thin films of nickel for decorative or protective purposes is known. In fact, Spencer in his article in The Metal Industry, London, January 22, 1937, on page 143, under the sub-title "Heat Treatment" clearly points out why electrolytic nickel would be unsatisfactory for use as anodes. Spencer states

"The pure nickel used in industry in the United States is supplied in the form of electrodeposited plates or sheets about one-fourth inch in thickness and cut up in squares of suitable size. It has the typical structure of such deposits in that it consists of groupings of parallel elongated crystals, their size and shape apparently being dependent on the uniformity or non-uniformity of the electric current, composition of the solution, temperature, and other such factors. Any change in these will alter the rate of deposition and the crystal size. If the current is stopped, metal deposition will cease, and re-solution of nickel from the cathode may occur, or copper or other metal impurities in the solution may deposit by immersion, with formation of a film of oxides or basic salts on the surface. When deposition is resumed, a new layer of crystals of different orientation will be formed, probably with weak adherence to the underlying metal. This is one reason why cathode sheet nickel would be unsatisfactory for use as anodes.

* * * * * * *

"* * * Because of the internal stresses developed in deposition, it should be more easily attacked by the solution than annealed or heat-treated metal. On the other hand, since the stresses probably are not uniform throughout the piece, the corrosion would be uneven, and an undesirable amount of anode scrap would be formed with a considerable quantity of loose metallic particles which would interfere with smooth plating. It would seem, therefore, that cathode sheets should be given a slight annealing treatment in order to relieve such stresses and produce a metal as uniform in grain size as possible. From a commercial point of view it is questionable whether the cost of depositing such an anode and annealing it would be low enough to make it economically practicable."

While no organization officially has agreed upon the specifications with which nickel anodes must comply to be acceptable by the trade, there is general agreement among not only the users of nickel anodes, but also the producers thereof, regarding certain characteristics which a nickel anode must have to be acceptable by the trade. Thus, it is agreed that a nickel anode should have a high degree of purity and be substantially free from or at least only contain a practical minimum of those elements, such as copper, manganese, iron and zinc, which enter the bath and are plated on the article together with the nickel. It is claimed that an amount of copper and/or iron above a certain percentage in a nickel electrodeposit will cause dark streaks. Furthermore, the presence of manganese is considered to be highly detrimental in that it is considered to affect the corrosion resistance of the nickel deposit adversely. Thus, some experts in the art specify that an anode shall contain less than 0.005 per cent manganese.

In addition, the anode should be soluble in the bath under the plating conditions used and have a high anode efficiency which means that the pH of the electrolyte can be easily maintained. In maintaining the operating pH of a nickel electroplating bath, it is always desirable to do this by adding sulphuric acid to the bath

to bring the pH down to the level required rather than adding basic salts, such as nickel hydrate or carbonate, to raise the pH. In order that the condition of gradually rising pH shall exist during the plating operation, anode efficiency must be slightly higher than the cathode efficiency.

In addition a nickel anode must dissolve with a minimum amount of sludge remaining and the nature of the sludge should be such that all of it can be retained by an anode bag. If bags are not being used, the sludge should adhere to the anode and build up in sufficient thickness in order to entrap any small particles of loose metallics which may come from the anode. Furthermore, when a layer of sludge does drop off, it should be dense and heavy so that it immediately sinks to the bottom of the plating tank. However, in all first class plating shops the injurious effect on the deposit, which can readily be caused by particles of metallics and sludge, is recognized. Consequently, all types of anodes are bagged and at the same time the electrolyte is continuously or intermittently filtered through a filter medium with the result that the electrolyte is practically free from suspended matter.

The art has agreed that a nickel anode should dissolve in such a manner that practically no metallic particles are evolved since it has definitely been proven that these metallic particles can cause rough work. The commercial importance of percentages of loose nickel is perhaps better realized when it is appreciated that certain large purchasers of nickel anodes have purchased anodes on a specification of a maximum loose nickel of 0.04 per cent of the total weight of anode dissolved.

A nickel anode should dissolve smoothly and uniformly, having a good appearance throughout the corrosion period. If the anode does not corrode smoothly in all probability an undesirable amount of loose nickel is being set free at the anode since these two phenomena are closely associated with each other.

It is recognized in the plating industry that various compositions of anodes have definite pH limits of smooth corrosion. Above these limits the anodes cease to corrode smoothly and uniformly. In many instances they become covered with a soft, spongy, metallic "hide" or "skin" on the surface or the metal may remain hard and firm but selective corrosion takes place, causing furrows or grooves in the anode face. The pH at which the surface becomes rough or spongy has been defined as the "upper limit of smooth corrosion" or its "activity limit."

A nickel anode should be free from metallurgical defects, such as longitudinal or transverse cracks, commonly termed "fire cracks," and slag pockets or gas holes.

During the normal corrosion of the anode it has been found that the areas around such defects corrode at a slightly higher rate than the body of the anode with the result that the bar may corrode completely through at these spots, causing an unused section to fall to the bottom of the tank. Therefore, since it is highly desirable and economical to have as little scrap loss as possible, the anode bars should be free of such defects mentioned above.

Likewise, a nickel anode should have a size and shape so that a maximum amount of surface is exposed and at the same time require only a small amount of tank space. The shape and size should also be such as to be easily handled and to be attached to the anode bus bar by means of anode hooks. For the above reasons the elliptical shape of the anodes now being used in the trade is pretty much standardized. By this shape it is possible to produce a section which contains about one pound of nickel per linear inch.

There are three main types of anodes being used in large tonnages in the plating industry today. These are the rolled carbon and rolled "depolarized," both 99 per cent plus, which are elliptical in shape and are of such a section that the weight is approximately one pound per linear inch, the 99 per cent plus cast carbon anodes which are also elliptical in shape but have a slightly larger cross section and weigh more than one pound per inch, and electrolytic nickel anodes.

Finally, a nickel anode should have a good, clean surface and be free from mechanical and metallurgical defects in the "as purchased" condition. The surface layer of an anode should be prepared either by pickling or "deskinning" (activating) so that it begins to dissolve immediately when placed in the plating circuit.

From the foregoing discussion it will be appreciated that the desirable characteristics and the characteristics of nickel anodes required by the art are entirely different from the desirable and required characteristics of protective and/or decorative nickel electrodeposits. For these reasons, nickel anodes for use in the production of protective and/or decorative nickel electroplate have contained addition agents and have not been of the highest nickel content possible.

While the art has recognized the advantages resulting from the incorporation of small controlled amounts of substances other than nickel in nickel anodes, for example, oxygen, copper, sulphur, silicon etc., on the other hand, in the production of electrolytic nickel anodes in the past, every attempt has been made to exclude from the cathode deposit all elements except nickel and cobalt. This has resulted in an electrolytic nickel which, with the years, has become purer until today electrolytic nickel has a purity greater than 99.80% (nickel plus cobalt) and is devoid of sulphur. Therefore, a problem confronted the experts in the art, to wit: the incorporation of sulphur in electrodeposited nickel anodes without recourse to additional steps of melting electrolytic nickel, adding sulphur to the molten nickel and casting a sulphur-containing nickel ingot suitable for reduction to anodes. In other words, if sulphur could be incorporated directly in an electrolytic nickel anode during the deposition of the nickel, a more economic process for producing active nickel anodes, having good corrosion and satisfactory sludge characteristics would be achieved.

I have discovered that sulphur can be incorporated in an electrolytic nickel anode during the deposition of the nickel.

It is an object of the present invention to provide a means for producing electrolytic nickel containing sulphur.

It is another object of the present invention to provide a means for producing electrolytic nickel containing sulphur within critical limits.

The present invention also contemplates a novel nickel electrolyte from which nickel containing sulphur can be electrodeposited.

It is a further object of the present invention to provide electrolytic nickel anodes containing sulphur within critical limits.

Other objects and advantages of the present

invention will become apparent from the following description and drawing in which:

Figure 1 is a photomicrograph of a transverse section of conventional electrolytic nickel and

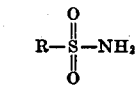
Figure 2 is a photomicrograph of a transverse section of novel sulphur-containing active electrolytic nickel.

In its broadest aspect the present invention contemplates incorporating in the usual or conventional or standard or other electrolytic bath for the production of electrolytically deposited nickel anodes, i. e., cathode-nickel anodes, an electrolyte soluble substance containing sulphur which during the electrodeposition of nickel will deposit sulphur with the nickel. While the particular form in which sulphur must be present in a nickel anode to provide the good corrosion and activity during subsequent electroplating is not generally known, I have found that certain sulphur-containing materials give satisfactory results whereas others do not. Thus, for example, among the inorganic sulphur-containing compounds which are ineffective is sodium pyrosulphate. On the other hand, sodium thiosulphate is effective. Among the organic substances which are ineffective although containing sulphur, are trional and sulphonal while among the effective materials are thio-urea, methylene blue and others.

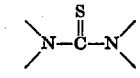
From my investigations it would appear that the conditions under which the electrodeposition is carried out has a bearing upon the amount of sulphur which is deposited together with the nickel. For example, nickel deposited at low pH and high current density from an electrolyte containing sodium sulphite contains no sulphur whereas nickel deposited at high pH and low current density from an electrolyte containing sodium sulphite contains about 0.015% sulphur. On the other hand, nickel electrodeposited at low pH and high cathode current density and nickel electrodeposited at high pH and low cathode current density from nickel electrolytes containing sodium pyrosulphate contain practically no sulphur and corroded unsatisfactorily at pH 4.0 (quinhydrone). When a deposit containing 0.015% sulphur such as that obtained from an electrolyte containing sodium sulphite is corroded under standard testing conditions at a pH of about 4.0 as determined by the quinhydrone electrode the corrosion is unsatisfactory. Nickel deposited at low pH and high current density from an electrolyte containing sodium bisulphite contained about 0.11% sulphur whereas nickel deposited from a similar electrolyte at high pH and low current density contained no sulphur and in both cases, the corrosion of the nickel anode thus produced was poor. In contrast to the foregoing, nickel deposits made from a bath containing sodium thiosulphate and deposited at low pH and high current density or high pH and low current density both contained sulphur and corroded anodically in a satisfactory manner. Thus it will be seen that sulphur is not deposited with equal facility from all sulphur containing inorganic materials. Nor is the mere presence of sulphur an assurance that the nickel deposit containing the sulphur will corrode anodically in a satisfactory manner.

It would appear that the activity at a high pH such as pH 4.0 (quinhydrone) is dependent not so much upon the presence of sulphur but upon the presence of at least a critical amount. Thus, during these investigations it has appeared that in order to have a good activity at high pH such as pH 5.5 (quinhydrone) it is necessary to have a minimum sulphur content in the cathode nickel anodes of at least about 0.011% and a maximum sulphur content in the cathode nickel anodes of about 0.05 to about 0.06%.

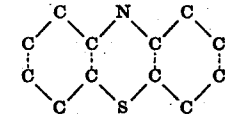
Illustrative of sulphur-containing compounds which may be employed for the purpose of introducing into cathode nickel sufficient sulphur to ensure that the cathode nickel when employed as anode for electroplating for protective and decorative purposes at high pH such as pH 5.5 (quinhydrone) will have good activity are 5 types of sulphur-containing compounds. These sulphur compounds may be classified as (1) sulphonamides or substituted sulphonamides having the type formula



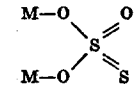
where R is an aromatic radical such as that of benzene and its homologues and naphthalene and its homologues. (2) thio-urea and substituted thio-urea having the basic structure



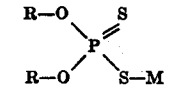
(3) phenthiazine compounds such as methylene blue having the basic structure



(4) thiosulphates having a structure considered to be



such as sodium thiosulphate and (5) dithiophosphates considered to have the basic structure



(where R is a cyclic radical such as the cresol or phenol radical or where R may be an alicyclic radical) and M is an alkali metal such as the dithiophosphates well known to the art of concentrating minerals by flotation. These phosphorus and sulphur containing addition agents may be prepared from substances containing a hydroxyl group, such as alcohols or phenols or from substances containing carboxyl groups (—COOH) the aldehyde group, (—COH) or the ketone group, (—CO).

In the preparation of cathode nickel containing sulphur for direct use as anode in the electrodeposition of nickel for protective and/or decorative purposes it has been found that 4 factors, to wit: concentration of sulphur-containing addition compound, cathode current density, pH of the bath and temperature; influence the amount of sulphur deposited with the cathode nickel. Of course, solubility of the sulphur-bearing addition agent in the electrolyte also has an effect upon the amount of sulphur introduced into the cathode nickel. Furthermore, when the sulphur-bearing addition agent forms insoluble precipitates or an oily reaction product with the con-

stituents of the electroplating bath, unsatisfactory results are usually obtained. Thus, when insoluble reaction products or oily reaction products are formed with the constituents of the bath in some instances these reaction products migrate to the cathode and the cathode nickel thus produced may be very rough and porous due to the presence of the precipitated reaction products in the electrolyte.

The four factors enumerated above affect the sulphur content of cathode nickel when deposited from a bath containing a sulphonamide or substituted sulphonamide generally as follows:

The sulphur content of the cathode nickel increases first rather rapidly with the concentration until the concentration of soluble sulphonamide in the electrolyte reaches a value of about 0.35 gram per liter. Thereafter the sulphur content of the cathode nickel increases quite slowly with increased concentration of sulphonamide. The sulphur content of cathode nickel is affected negligibly by the cathode current density when this class of sulphur bearing compound is employed. The sulphur content of cathode nickel varies with the pH being high at low pH and low at high pH when sulphonamides or substituted sulphonamides are employed. In the presence of sulphonamides or substituted sulphonamides the sulphur content of cathode nickel increases with decrease in temperature. The foregoing is clearly evident from the following tabulations:

Effect of Concentration of Sulphur-Bearing Addition Agent (Sulphonamides or Substituted Sulphonamides)

Conditions.—pH, 2.5 (quinhydrone). Cathode current density, 30 amperes per square foot. Temperature, 45° C.

Concentration of sulphur-bearing addition agent, in grams per liter	Per cent sulphur in cathode nickel	Activity of cathode nickel at pH 5.5 (quinhydrone)
0.05	0.012	Passive
0.15	0.034	Fair
0.35	0.042	Good
0.50	0.045	Good
1.00	0.047	Good

Effect of Current Density

Conditions.—pH, 2.5 (quinhydrone). Temperature, 45° C. Concentration of sulphur bearing addition compound, 1.00 gram per liter.

Current density (amperes square foot)	Per cent sulphur in cathode nickel	Activity of cathode nickel at pH 5.5 (quinhydrone)
10	0.045	Good
30	0.047	Good
50	0.049	Good

Effect of Variation of pH

Conditions.—Cathode current density, 30 amperes per square foot. Temperature, 45° C. Concentration of sulphur bearing addition agent 1.00 gram per liter.

pH (quinhydrone)	Per cent sulphur in cathode nickel	Activity of cathode nickel at pH 5.5 (quinhydrone)
2.0	0.066	Good
2.5	0.047	Good
4.0	0.035	Fair
5.3	0.025	Passive

Low pH—High Current Density

Conditions.—Low pH, pH 2.5. High current density, 30 amperes per square foot. Temperature, 45° C. Concentration of sulphur-bearing addition agent, 0.25 grams per liter of electrolyte. Plating time, 48 hours.

Sulphur bearing addition agent	Per cent sulphur in cathode nickel	Activity of cathode nickel at pH 5.5 (quinhydrone)
Para toluene sulphonamide	0.049	Good
Ortho toluene sulphonamide	0.044	Good
Dichloramine T (ortho or para toluene sulphondichloramine)[1].	0.011	Fair
Benzene sulfonamide	0.057	Good

[1] Dichloramine T has a low solubility in solutions of low pH.

High pH—Low Current Density

Conditions.—pH, 5.5 (quinhydrone). Cathode current density, 15 amperes per square foot. Temperature, 45° C. Concentration of sulphur-bearing addition agent, 0.25 gram per liter. Plating time, 100 hours.

Sulphur-bearing addition agent	Percent sulphur in cathode nickel	Activity at pH 5.5 (quinhydrone)
Para toluene sulphonamide	0.029	Good
Ortho toluene sulphonamide	0.020	Good
Dichloramine T (ortho or para toluene sulphondichloramine).	0.032	Good
Benzene sulphonamide	0.036	Good

Effect of Variation in Temperature

Conditions.—pH, 2.5 (quinhydrone). Cathode current density, 38 amperes per square foot. Concentration of sulphur-bearing addition agent, 1.00 gram per liter.

Temperature, ° C.	Percent sulphur in cathode nickel	Activity of cathode nickel at pH 5.5 (quinhydrone)
30	0.068	Very good
45	0.047	Good

The sulphur content of cathode nickel produced in an electrolyte containing thio-urea or substituted thio-urea varies (1) substantially linearly with the concentration of sulphur bearing addition compound; (2) with the current density. The sulphur content of cathode nickel increases slightly with increased pH and with decrease in temperature when thio-urea or substituted thio-urea is employed.

Effect of Variation in Concentration of Sulphur Bearing Addition Agent

Conditions.—pH, 2.5 (quinhydrone). Cathode current density 30 amperes per square foot. Temperature, 50° C.

Concentration of thiourea in grams per liter	Sulphur content of cathode nickel
0.05	0.109
0.10	0.172
0.15	0.300
0.20	0.410
0.25	0.495

Effect of Variation in Current Density

Conditions.—pH, 2.5 (quinhydrone). Temperature, 50° C. Concentration of thio-urea, 0.10 gram per liter.

Current density, amperes per square foot	Percent sulphur in cathode nickel
10	0.422
30	0.172
50	0.300

Effect of Variations in pH

Conditions.—pH, 2.5 (quinhydrone). Cathode current density, 30 amperes per square foot. Temperature, 50° C. Concentration of thio-urea, 0.10 gram per liter.

pH (quinhydrone)	Percent sulphur in cathode nickel
1.5	0.669
2.5	0.172
4.2	0.184
5.5	0.202

Effect of Variation in Temperature

Conditions.—pH, 2.5 (quinhydrone). Cathode current density, 30 amperes per square foot. Concentration of thio-urea, 0.10 gram per liter.

Temperature, ° C.	Percent sulphur in cathode nickel
30	0.225
50	0.172

The sulphur content of cathode nickel electrodeposited in baths containing substituted phenthiazine compounds such as methylene blue (1) varies directly with the concentration of the phenthiazine compound; (2) decreases with increase of cathode current density; (3) increases slightly with increase or decrease of pH from a median pH and increases with a rise in temperature.

Effect of Variation in Concentration of Sulphur-Bearing Addition Agent

Conditions.—pH, 2.5 (quinhydrone). Cathode current density 30 amperes per square foot. Temperature, 40° C.

Concentration of Methylene Blue, grams per liter	Per cent sulphur in cathode nickel
0.05	0.022
0.10	0.034
0.15	0.055
0.20	0.070
0.25	0.083

Effect of Variation in Cathode Current Density

Conditions.—pH, 2.5 (quinhydrone). Temperature, 40° C. Concentration of Methylene Blue, 0.25 gram per liter.

Cathode current density, amperes per square foot	Percent sulphur in cathode nickel
10	0.115
30	0.083
50	0.074

Effect of Variation in pH

Conditions.—Cathode current density, 30 amperes per square foot. Temperature, 40° C. Concentration of Methylene Blue, 0.25 gram per liter.

pH (quinhydrone)	Percent sulphur in cathode nickel
1.8	0.098
2.6	0.083
4.2	0.081
5.6	0.111

Effect of Variation in Temperature

Conditions.—pH, 2.5 (quinhydrone). Cathode current density 30 amperes per square foot. Concentration of Methylene Blue, 0.25 gram per liter.

Temperature, ° C.	Per cent sulphur in cathode nickel
[1] 28	0.048
40	0.083

[1] Addition agent crystallized out in part from the colder solution.

The sulphur content of cathode nickel produced in electrolytes containing sodium thiosulphate (1) varies directly with the concentration, (2) is slightly affected by cathode current density, (3) varies considerably with high or low pH from a median pH, and (4) increases slightly with decrease in temperature.

Effect of Variation in Concentration of Sulphur-Bearing Addition Agent

Conditions.—pH, 2.5 (quinhydrone). Cathode current density, 30 amperes per square foot. Temperature, 40° C.

Concentration of thiosulphate in grams per liter	Per cent sulphur in cathode nickel
0.05	0.040
0.10	0.081
0.15	0.104
0.20	0.128
0.25	0.142

Effect of Variation in Current Density

Conditions.—pH, 2.5 (quinhydrone). Temperature, 40° C. Concentration of thiosulphate, 0.10 gram per liter.

Current density in amperes per square foot	Per cent sulphur and cathode nickel
10	0.127
30	0.081
50	0.101

Effect of Variation in pH

Conditions.—Cathode current density, 30 amperes per square foot. Temperature, 40° C. Concentration of thiosulphate, 0.10 gram per liter.

pH (quinhydrone)	Percent sulphur in cathode nickel
1.9	0.139
2.5	0.081
4.0	0.060
5.5	0.116

Effect of Variation in Temperature

Conditions.—pH, 2.5 (quinhydrone). Cathode current density, 30 amperes per square foot. Concentration of thiosulphate, 0.10 gram per liter.

Temperature, ° C.	Percent sulphur in cathode nickel
29	0.092
40	0.081

The sulphur content of cathode nickel produced in electrolytes containing soluble dithiophosphates (1) varies directly with the concentration of the dithiophosphate; (2) decreases with increase of cathode current density; (3) increases with increase in pH; (4) increases with temperatures.

Effect of Variation in Concentration of Addition Agent

Conditions.—pH, 2.6 (quinhydrone). Cathode current density, 30 amperes per square foot. Temperature, 40° C.

Concentration of dithiophosphate (sodium cresol dithiophosphate), grams per liter	Per cent sulphur in cathode nickel	Per cent phosphorus in cathode nickel
0.05	0.010	0.006
0.10	0.034	0.010
0.15	0.052	0.030
0.20	0.062	0.037
0.25	0.092	0.048

Effect of Variation in Cathode Current Density

Conditions.—pH, 2.6 (quinhydrone). Temperature, 40° C. Concentration of dithiophosphate, 0.20 gram per liter.

Cathode current density in amperes per square foot	Percent sulphur in cathode nickel	Percent phosphorus in cathode nickel
10	0.089	0.076
30	0.062	0.037
50	0.058	0.049

Effect of Variation in pH

Conditions.—Cathode current density, 30 amperes per square foot. Temperature, 40° C. Concentration of dithiophosphate, 0.20 gram per liter.

pH (quinhydrone)	Percent sulphur in cathode nickel	Percent phosphorus in cathode nickel
1.7	0.054	0.050
2.6	0.062	0.037
4.1	0.068	0.042
5.5	0.088	0.060

Effect of Variation in Temperature

Conditions.—pH, 2.6 (quinhydrone). Cathode current density, 30 amperes per square foot. Concentration of dithiophosphate, 0.20 gram per liter.

Temperature, ° C.	Per cent sulphur in cathode nickel	Per cent phosphorus in cathode nickel
21	0.050	0.056
40	0.062	0.037

The preferred operating conditions for each of the foregoing classes of sulphur-bearing addition compounds are summarized in the following tabulations:

Sulphonamides and substituted sulphonamides

pH—about 2.0 to about 2.5 (quinhydrone)
Current density—about 10 to about 50 amperes per square foot
Temperature—about 25° C. to about 40° C.
Concentration of sulphonamide—about 1.00 gram per liter

Thio-urea and substituted thio-ureas

pH—about 2.2 to about 3.0 (quinhydrone)
Current density—about 10 to about 50 amperes per square foot
Temperature—about 30° to about 50° C.
Concentration of sulphur-bearing addition compound—about 0.02 to about 0.10 gram per liter

Substituted phenthiazine addition agents

pH—about 2.5 to about 4.5 (quinhydrone)
Current density—about 10 to about 50 amperes per square foot
Temperature—about 30 to about 50° C.
Concentration of substituted phenthiazine compound—about 0.10 to about 0.20 gram per liter

Thiosulphate addition agents

pH—about 2.5 to about 4.5 (quinhydrone)
Current density—about 10 to about 50 amperes per square foot
Temperature—about 20° C. to about 50° C.
Concentration of thiosulphate—about 0.10 to about 0.20 gram per liter

Dithiophosphate addition agents

pH—about 1.7 to about 5.5 (quinhydrone)
Current density—about 10 to about 50 amperes per square foot
Temperature—about 20° to about 40° C.
Concentration of dithiophosphate—about 0.10 to about 0.25 gram per liter

From the foregoing it will be appreciated that sulphur-bearing cathodic nickel can be electrodeposited from conventional nickel electrolytes such as electrolytes containing about 84 grams of nickel per liter, about 13 to 14 grams of chloride per liter and about 14 to 15 grams of boric acid per liter and containing about 0.2 of a gram to about 1 gram per liter of sulphur-bearing electrolyte soluble compound. The electrodeposition of the novel sulphur-bearing cathodic nickel can be carried out at a pH of about 1.7 to about 5.5 at a temperature of about 20 to about 50° C. at a current density of about 10 to about 50 amperes per square foot.

It would appear that the sulphur present in the electrolytically produced nickel anode should be present in the anode principally in the sulphide form. I have found that it would appear that those anodes which have satisfactory activity at high pH [pH 4.0 (Q) and above] when analyzed for total sulphur by the acid evolution method contain sulphur in the sulphide form. That is to say for example, the total sulphur as determined as barium sulphate was 0.045% and the sulphur determined by acid evolution was 0.041 to 0.045%. It would appear from these results that all, or practically all the sulphur of the electrolytically produced nickel anodes was in sulphide form. These anodes had satisfactory activity at pH 4(Q) and above, corroded smoothly and produced small amounts of sludge containing small amounts of metallic nickel. Consequently, such anodes are acceptable to the trade from all technical considerations.

The novel sulphur-bearing cathodic nickel or

electrolytic nickel produced in accordance with the foregoing disclosure has a novel microstructure which readily enables experts in the art to differentiate this novel sulphur-containing electrolytic nickel from conventional sulphur-free electrolytic nickel. The difference in microstructure can be readily discerned by study of the drawing, Figs. 1 and 2. Figure 1 is a reproduction of a photomicrograph of conventional sulphur-free electrolytic or cathodic nickel electrodeposited under the customary and conventional conditions of electrolytic recovery of nickel. The photomicrograph of Fig. 1. was taken at a magnification of 500 diameters of a transverse section of regular conventional sulphur-free electrolytic or cathodic nickel and is a typical specimen of regular or conventional sulphur-free electrolytic nickel. Fig. 2 is a reproduction of a photomicrograph taken at 500 diameters magnification of a transverse section of the novel active sulphur-bearing electrolytic or cathodic nickel, and is typical of the novel active sulphur-bearing electrolytic nickel produced in accordance with the foregoing disclosure.

The regular or conventional sulphur-free electrolytic or cathodic nickel was electrodeposited from a bath containing about 40 grams per liter of nickel, about 35 grams per liter of Na_2SO_4 and about 20 grams per liter of boric acid at a pH of about 5.0(Q) at a temperature of about 57° C. and a current density of about 12 amperes per square foot.

The novel active sulphur-bearing electrolytic or cathodic nickel of Figure 2 can be produced in an electrolyte having about the same composition as the foregoing, but containing about 1 gram per liter of ortho benzoyl sulphonamide. The novel active sulphur-bearing cathodic nickel of Figure 2 had the following analysis:

Sulphur	About 0.030% as sulphide
Copper	About 0.026%
Iron	About 0.045%
Cobalt	About 0.48%
Nickel	Balance

In other words, the novel active sulphur-bearing cathodic nickel produced in accordance with the foregoing disclosure contains about 0.030% sulphur principally as the sulphide and the balance principally nickel except for a small amount of cobalt and incidental impurities. A typical analysis of conventional or regular sulphur-free electrolytic or cathodic nickel is as follows:

Copper per cent	0.0025 to 0.01
Carbon	None
Iron per cent	Trace to 0.01
Manganese	None
Sulphur	Trace
Nickel including incidental amounts of cobalt	Balance

A comparison of Figs. 1 and 2 makes manifest the differences in microstructure which exist between regular sulphur-free electrolytic nickel and the novel active sulphur-bearing electrolytic nickel of the present invention. In Fig. 2 the presence of large amounts of nickel sulphide is plainly revealed and the photomicrograph shows that the nickel sulphide is mainly concentrated in the grain boundaries. There is no analogous structure discernible in the reproduction of the photomicrograph of a regular sulphur-free electrolytic nickel provided in Fig. 2. Thus, an inspection of the microstructure of the novel active sulphur-bearing electrolytic nickel of the present invention provides a ready means for distinguishing this novel sulphur-bearing electrolytic nickel from conventional sulphur-free electrolytic nickel.

As illustrative of the manner in which my novel electrolytic nickel anodes containing sulphur may be produced, the following typical examples of the electrolyte, quantities of addition agents and the operating conditions under which such sulphur-containing electrolytic nickel anodes may be produced are provided in the following illustrative examples.

Example I

The anodes were deposited from a bath substantially equivalent to the conventional electrolyte commonly employed in the industry for this purpose. That is to say, an electrolyte was employed containing about 84.46 grams per liter of nickel, about 13.85 grams per liter of chloride, and about 14.96 grams per liter of boric acid. In other words, the electrolyte contained a source of nickel, an anode corroding agent and a buffer. When an insoluble anode is used the anode corroding agent need not be present. Under such conditions conventional salts such as sodium sulphate may be incorporated to increase the conductivity of the electrolyte. To this electrolyte was added about 0.25 gram per liter of the sulphur-containing addition agent, in this instance sodium thiosulphate. The distance from the anode to the cathode was about 2 inches. The temperature during electrodeposition was between about 40 and about 45° C. A low pH of about 1.8 to about 3.0 was employed and the electrolyte was agitated by an air lift pump. An anode current density of 8 amperes per square foot and a high cathode current density of 27 amperes per square foot was employed. An electrodeposit of nickel weighing about 130 grams was obtained. Upon testing this cathodic nickel as an anode at a pH of about 4.0, it was found that this cathodic nickel deposited from a bath containing sodium thiosulphate had satisfactory activity and satisfactory corrosion characteristics. Corrosion at pH 5.5 (Q) showed that after 18 hours the metal of the anode was still hard and firm, the anode had satisfactory activity and satisfactory corrosion properties. The anode produced cathodically in the bath containing sodium thiosulphate contained about 0.11% of sulphur practically all of which was present in a form reacting with HCl to form H_2S.

Example II

From the standard or conventional electrolyte containing about 0.25 gram per liter of orthobenzoyl-sulphonimide a deposit of about 116 grams of cathodic nickel was obtained after a run of about 46 hours. The pH of the electrolyte during this period of electrodeposition was about 1.9 to about 2.6. An anode current density of about 8 amperes per square foot and a cathode current density of about 27 amperes per square foot were employed. From the foregoing it will be seen that the electrolytic nickel anode thus produced was produced under conditions of low pH and high current density. This cathodic nickel was then corroded as an anode at a pH of about 4.0 (Q) at a temperature of about 40 to 45° C. at an anode current density of about 15 amperes per square foot and a cathode current density of about 4 amperes per square foot in an electrolyte containing 81.70 grams per liter of nickel, 13.12 grams per liter of chloride and 40.10 grams per liter of boric acid. The pH during the

corrosion ranged from 4.0 to 4.3 (Q) and the anode lost about 38 grams during a corrosion of about 22 hours. The surface of the anode was covered completely with a thin black film of sludge. The anodic metal was hard and firm at all points. The corrosion of the face of the anode was smooth and the anode was highly active. From all technical considerations this anode was highly satisfactory. This anode likewise was tested for corrosion characteristics in a hot Watts type test solution having a pH of about 5.5 (Q) at the initiation of the corrosion. After 22 hours of corrosion the anode was still active, was completely covered with a thin black film of sludge, the metal was hard and firm at all points and the corrosion of the face was smooth. Thus, this anode is considered to be highly active at high pH's above pH 4.0 (Q). The sulphur content of this anode was 0.054%.

EXAMPLE III

In the same electrolyte and under the same conditions as set forth hereinbefore in Example 1, an electrolytic anode was prepared from a standard electrolyte containing about 0.25 gram per liter of phenthiazine compound, to wit: Methylene blue in the form of its chloride. The pH of the electrolyte containing methylene blue was 1.8 at the start of the electrodeposition. After 18 hours of electrodeposition the pH of the electrolyte had risen to 2.3. After 8 hours further electrodeposition, the pH had risen to 2.6. A small amount of sulphuric acid was added to lower the pH and after a further 16 hours of electrodeposition, the pH of the electrolyte was 3.5.

Upon corroding the cathodic nickel produced by electrodeposition from a standard electrolyte containing about 0.25 gram per liter of methylene blue as its chloride initially for 22 hours as an anode, inspection of the corroded anode showed that the surface was dark all over and the activity of the anode good. Cathodic nickel produced in the bath containing methylene blue was then corroded in a hot Watts type electrolyte having a pH of about 5.5 (Q) at the start of the corrosion. After 22 hours of corrosion, the anode was covered with sludge but was still active. It is manifest therefore, that cathodic nickel electrodeposited from an electrolyte, containing methylene blue has good activity and is satisfactory for use as an anode in the electrodeposition of protective, decorative or utilitarian films of nickel. The electrodeposited nickel produced in the bath containing methylene blue contained about 0.104% sulphur.

EXAMPLE IV

A second anode was prepared by cathodic deposition of nickel from a standard electrolyte containing 0.25 gram per liter of methylene blue. The cathodic nickel so obtained contained about 0.023 gram of sulphur present principally as the sulphide. This cathodic nickel upon corrosion at pH 4.0 and pH 5.5 (Q) made it manifest that such cathodic nickel is suitable for use as plating anodes in the deposition of protective, decorative and/or utilitarian films of nickel. This second methylene blue anode had good activity, satisfactory corrosion and only produced amounts of sludge which are acceptable to the art.

EXAMPLE V

The same standard electrolyte was employed as employed in Example 1 to which was added 0.25 gram per liter of thio-urea. The cathodic nickel so produced was corroded at about pH 4.0 (Q) employing an anode current density of about 15 amperes per square foot. The anode was completely covered with a thin black film of sludge indicating uniform corrosion. A similar portion of cathodic nickel produced from a bath containing 0.25 gram per liter of thio-urea was likewise tested for activity at pH 5.5 (Q). After 18 hours the metal was still hard and firm. The anode had corroded uniformly and was completely covered with a black sludge. Thus it is apparent that cathodic nickel produced by electrodeposition from standard electrolytes containing 0.25 gram of thio-urea per liter initially give satisfactory results when employed as anodes at high pH's, such as pH 4 and above. The aforesaid anode contained 0.46% sulphur, practically all of which was present in form reacting with HCl to produce H_2S.

EXAMPLE VI

Cathodic nickel was deposited under the aforedescribed conditions at low pH and high current density from a standard electrolyte containing initially about 0.25 gram of a dithiophosphate sold under the trade name of "Sodium Aerofloat." The cathodic nickel thus produced when corroded anodically at pH's 4.0 and 5.5 (Q) showed good activity and highly satisfactory corrosion characteristics. The sulphur content of this anode was about 0.175 and the sulphur was present principally as a sulphide. The phosphorus content of this anode was about 0.103.

Other massive deposits suitable for use as anodes and corroding very satisfactorily at high pH such as 5.5 (Q) were obtained from a standard nickel electrolyte containing a dithiophosphate. An anode produced at high pH and low current density contained about 0.30% sulphur, about 0.133% phosphorus and corroded very satisfactorily at pH 5.5 (Q).

EXAMPLE VII

Cathodic nickel for use as an anode in nickel electroplating baths both for the deposition of common gray nickel and "bright" nickel may be deposited from conventional nickel electrolytes containing initially about 0.25 gram per liter of "Thioflavine S." As those skilled in the art know, "Thioflavine S" is a methyl derivative of sulphonated primuline, and usually comes on the market as the sodium salt of the sulphonate. When cathodic nickel produced in a bath containing thioflavine S is corroded anodically at pH's 4.0 and 5.5 (Q), it is manifest that such metal is suitable for use as anode in nickel electroplating. This nickel is active at both pH 4.0 and 5.5 and the anode becomes covered with a black sludge.

Similar sulphur-containing materials derived from dehydro-thio-para-toluidine such as thioflavine T may likewise be employed with equally satisfactory results. The anode produced cathodically in the bath containing thioflavine S contained about 0.078% copper and about 0.033% sulphur, the sulphur being present principally as a sulphide.

The anodes produced as described hereinbefore had a thickness of about 0.2 centimeter or, in other words, about 0.08 inch. As those skilled in the art will readily understand, such deposits are many times the thickness of the average film of nickel deposited for protective, decorative and/or utilitarian purposes, and considerably thicker

than even the thickest films produced by the prior art for protective, decorative and/or utilitarian purposes. In general, cathodic nickel suitable for use as anodes in plating conventional gray nickel or in electrodepositing "bright" nickel may be produced employing standard nickel electrolytes as the basic bath and operating at pHs of about 1.5 to about 6.0(Q), at anode current densities of about 3.0 to about 100 amperes per square foot and cathode current densities of about 5.0 to about 100 amperes per square foot. The electrodeposition of such cathodic nickel may be carried out at temperatures of about 20° F. to about 200° F., preferably with agitation of the electrolyte.

From the foregoing, those skilled in the art will appreciate that in distinct contrast to the thin foil-like films conventional in nickel electroplating for protective, decorative and/or utilitarian purposes, by the process of the present invention it is possible to produce massive deposits of electrolytic nickel containing sulphur. As a result thereof, it is now possible to provide the art with active cathode nickel anodes containing sulphur or containing sulphur and copper which corrode satisfactorily with production of small amounts of sludge containing small amounts of metallics and having good or excellent activity in electroplating baths of high pH. In other words, the conventional process for producing nickel anodes comprising producing electrolytic nickel substantially devoid of sulphur, melting the electrolytic nickel and adding sulphur to the molten nickel and finally casting the nickel containing sulphur as an ingot from which nickel anodes may be produced is no longer necessary, since it is now possible by means of the present invention to produce cathode nickel containing sulphur or cathode nickel containing copper and sulphur directly in the electro-recovering bath.

It is of interest that even those anodes produced from electrolytes containing such organic compounds as thio-urea, methylene blue, thioflavine S orthobenzoyl sulphonimide, or dithiophosphates are substantially devoid of carbon. This fact, coupled with the fact that the sulphur in the novel anodes of the present invention is present principally in the sulphide form is indicative that the sulphur is combined with the metal of the anode probably as a nickel or copper sulphide or as both.

The composition of the novel anodes is illustrated by the following examples:

EXAMPLE I

Constituents	Percent
Carbon	None
Iron	Trace
Manganese	Trace
Silicon	Trace
Sulphur	About 0.11
Copper	About 0.0025 to about 0.02
Nickel including incidental amounts of cobalt	Balance

EXAMPLE II

Constituents	Percent
Carbon	0.01
Iron	Trace
Manganese	Trace
Silicon	Trace
Sulphur	0.054
Copper	About 0.0025 to about 0.03
Nickel including incidental amounts of cobalt	Balance

EXAMPLE III

Constituents	Percent
Carbon	0.02
Iron	Trace
Manganese	Trace
Silicon	Trace
Sulphur	0.104
Copper	About 0.0025 to about 0.03
Nickel including incidental amounts of cobalt	Balance

I have found that sulphur-bearing electrolytic nickel having the composition given hereinafter is suitable for electroplating anodes.

Carbon	Trace to about 0.02
Iron	Trace
Manganese	Trace
Silicon	Trace
Sulphur	About 0.007 to about 0.11
Copper	About 0.0025 to about 0.03
Nickel including incidental amounts of cobalt	Balance

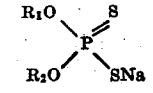
However, I prefer to employ a novel sulphur-containing electrolytic nickel having the composition given hereinafter for plating anodes:

Carbon	Trace
Iron	Trace
Manganese	Trace
Silicon	Trace
Sulphur	About 0.030 to about 0.050
Copper	About 0.010
Nickel including incidental amounts of cobalt	Balance

In the foregoing tabulation when the term "trace" is employed, I mean not more than about 0.01% iron, 0.005% manganese, and about 0.01% silicon.

It is to be understood that this disclosure is not to be limited to the exact details shown and described for obvious modifications will occur to those skilled in the art.

Thus, the term dithiophosphates is to be understood to include those phosphorus and sulphur-containing organic substances which are included in the type formula.



where R_1 and R_2 may be the hydrocarbon residues of aliphatic alcohols, carboxylic acids, aldehydes and ketones as well as the hydrocarbon residues of such members of the aromatic series as cresols, xylenols, naphthols and the like. It is likewise to be understood that as the sulphur content of the electrolyte decreases during the deposition of the electrolytic nickel containing sulphur, further amounts of the sulphur-containing addition agent as defined hereinbefore may be added to the fundamental nickel electrolyte if desirable. Furthermore, electrolytic nickel anodes as produced under the conditions described hereinbefore, may contain up to about 0.1% copper. In addition, the term electrolyte soluble as applied to sulphur-bearing substances suitable for use in the aforedescribed process means sulphur-bearing compounds which are soluble in the electrolyte at the pH at which electrodeposition of the cathodic nickel takes place. As a further means of defining the electrolyte soluble sulphur-bearing substances suitable for use in the aforedescribed process, the reduction potential at unit activity may be employed. That is to say, electrolyte soluble sulphur-bearing substances capa-

ble of ionizing to sulphur-containing radicals having a reduction potential to hydrogen sulphide at unit activity of not more than that of thiosulphate, for example, not more than about 0.64 volt may be employed. Moreover, while the present invention has been described in conjunction with conventional nickel electrolytes containing a source of nickel, an anode corroding agent and a buffer for use in conjunction with nickel anodes, those skilled in the art will appreciate that when insoluble anodes are employed and the electrolyte is the sole source of nickel, an anode corroding agent is not incorporated in the bath. Similarly, a suitable electrolyte is one containing about 40 to about 84 grams of nickel per liter in the form of electrolyte-soluble nickel salt.

A process for electrolytically producing nickel electroplating anodes containing sulphur is disclosed in the co-pending application Serial No. 295,255.

I claim:

1. A bath suitable for the electro-deposition of nickel anodes at least about 0.08 inch thick and containing sulphur within the range of 0.007 to 0.11% which comprises an aqueous electrolyte comprising essentially nickel ions, sulphate ions, chloride ions, borate ions and about 0.05 to 0.25 gram per liter of alkali metal thiosulphate, said bath having a pH of about 1.5 to 6.0 and being characterized by having the thiosulphate content of the entire bath present solely as alkali metal thiosulphate.

2. A bath suitable for the electro-deposition of nickel electro-plating anodes at least about 0.08 inch thick and containing sulphur within the range of 0.007 to 0.11% which comprises an aqueous electrolyte comprising essentially nickel ions, sulphate ions, chloride ions, borate ions and about 0.05 to 0.25 gram per liter of alkali metal thiosulphate, said bath having a pH of about 1.9 to 5.5 and characterized by having the thiosulphate content of the entire bath present solely as alkali metal thiosulphate.

3. A bath suitable for the electro-deposition of nickel anodes at least about 0.08 inch thick and containing sulphur within the range of 0.007 to 0.11% which comprises an aqueous electrolyte comprising essentially nickel ions, sulphate ions, chloride ions, borate ions and about 0.1 to 0.2 gram per liter of sodium thiosulphate, said bath having a pH of about 2.5 to 4.5 and characterized by having the thiosulphate content of the entire bath present solely as sodium thiosulphate.

4. A process for producing nickel anodes containing sulphur which comprises immersing an anode and a starting sheet as cathode in an aqueous electrolyte comprising essentially nickel ions, sulphate ions, chloride ions, borate ions and about 0.05 to 0.25 gram per liter of alkali metal thiosulphate, said electrolyte being characterized by having the thiosulphate content thereof present solely as alkali metal thiosulphate, maintaining said electrolyte at pH of about 1.5 to 6.0, and passing electric current at a cathode current density of about 5 to 100 amperes per square foot between said anode and cathode until a cathodic electro-deposit at least about 0.08 inch thick and containing about 0.007 to 0.11% sulphur is obtained, said cathodic electro-deposit being suitable in the as-deposited condition for subsequent use as an anode.

5. A process for producing nickel anodes containing sulphur which comprises immersing an anode and a starting sheet as cathode in an aqueous electrolyte comprising essentially nickel ions, sulphate ions, chloride ions, borate ions and about 0.05 to 0.25 gram per liter of alkali metal thiosulphate, maintaining said bath at pH of about 1.9 to 5.5, and passing electric current at a cathode current density of about 10 to about 50 amperes per square foot between said anode and cathode until a cathodic electro-deposit at least about 0.08 inch thick and containing about 0.007 to 0.11% sulphur is obtained, said cathodic electro-deposit being suitable in the as-deposited condition for subsequent use as an anode.

6. The process as set forth in claim 4 wherein the alkali thiosulphate is sodium thiosulphate.

7. The process as set forth in claim 5 wherein the alkali metal thiosulphate is sodium thiosulphate.

8. A process for producing nickel anodes containing sulphur which comprises immersing an anode and a starting sheet as cathode in an aqueous electrolyte comprising essentially nickel ions, sulphate ions, chloride ions, borate ions and about 0.1 to 0.2 gram per liter of sodium thiosulphate, maintaining said bath at pH of about 2.5 to 4.5, and passing electric current at a cathode current density of about 10 to 50 amperes per square foot between said anode and cathode until a cathodic electro-deposit at least about 0.08 inch thick and containing about 0.007 to 0.11% sulphur is obtained, said cathodic electro-deposit being suitable in the as-deposited condition for subsequent use as an anode.

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