ACID NICKEL ELECTROPLATING

Primary brighteners for acid nickel electroplating baths and processes are provided. The primary brightening additives are acrylic monomers selected from the group consisting of (1) an acrylic monomer of the formula:

\[ CH=C=O-\underset{R}{\overset{O}{\longrightarrow}}-O-C_{n}H_{2n}N(R')=X^- \]

wherein

- \( R \) is methyl or hydrogen,
- \( n \) is a positive whole integer of 1 to 3 inclusive,
- \( R' \) is alkyd of 1 to 4 carbon atoms,
- \( R'' \) is alkyd of 1 to 4 carbon atoms,

\[ -CH=CH-CH_2 \]
\[ -CH=CH-C=CH_2 \]
\[ -CH_2=CH-COOCH_3 \]
\[ -CH_2=CH-COOCH_3 \]
\[ -CH_2=CH-COOCH_3 \]
\[ -CH_2=CH-COOCH_3 \]
\[ -CH_2=CH-COOCH_3 \]

(2) a homopolymer of said acrylic monomer, and
(3) a copolymer of said acrylic monomer with at least one ethylenically unsaturated monomer selected from the group consisting of an \( \alpha,\beta \)-ethylenically unsaturated monomeric acid, an alkyl ester of said acid wherein the alkyl group is from 1 to 4 carbon atoms, acrylonitrile, acrylamide, methacrylamide, vinyl acetate, vinyl sulfone and vinyl pyridine, the molar ratio of said acrylic monomer to said unsaturated monomer being within the range of 0.9:0.1 to 0.1:0.9.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to acid nickel electroplating baths and processes.

Prior art

The electroplating of nickel from acid baths is old and well documented in the etching art. Nickel electrodeposits as plated from these baths, such as the well-known Watts' high chloride and fluoroborate type baths, are generally dull with a matte finish and are generally unattractive in appearance. To obtain bright deposits from such baths, it is necessary to add certain additives which assist in producing lustrous products with a good rate of brightening. Other advantages of such baths, such as leveling, may also be obtained.

Addition agents useful as brighteners in nickel plating

are generally divided into two classes on the basis of their predominant function. Primary brighteners are materials used in relatively low concentration which by themselves may or may not produce visible brightening action. However, some primary brighteners, when used alone, also produce some deleterious side effects such as deposit brittleness, narrow bright plate range and skip plating at low current densities. Secondary brighteners are materials which are usually used in combination with primary brighteners, but at a higher concentration. Secondary brighteners, by themselves, may produce some brightening action, but the deposits are usually not mirror bright and the rate of brightening is usually inadequate.

When primary and secondary brighteners are carefully selected, it is possible to obtain over a wide current density range ductile and leveled deposits at a good brightening rate.

In the patent art, U.S. Pat. 2,647,866 (issued to Henry Brown on Aug. 4, 1953) discloses the use of various pyridinium compounds, e.g., \( N \)-alkyl pyridinium bromide as primary additives for bright nickel plating. This patent also teaches the use of the pyridinium compounds in conjunction with organic sulfonic, sulfonamide and sulfonamide compounds which are the subjects of U.S. Pats. 2,191,813 and 2,466,677 also issued to Henry Brown. The use of various acetylenic compounds, e.g., 2-butyne-1,4-diol, as primary brighteners again used in conjunction with aromatic sulfonic compounds is the subject of U.S. Pat. 2,732,522 issued to Otto Kardo et al. on July 5, 1955.

More recently, U.S. Pat. 3,296,103 (issued to Frank Paschal on Jan. 3, 1967) teaches the use of compounds combining both pyridinium and acetylenic functions, e.g., \( \alpha \)-propargyl, 3-carboxamido pyridinium bromide as primary brighteners, again in conjunction with various sulfur compounds. Esters of unsaturated monocarboxylic acids, e.g., methyl acrylate used as primary brighteners is the subject of U.S. Pat. 2,690,996 (issued to Henry Brown on Oct. 5, 1954).

SUMMARY OF THE INVENTION

According to the present invention, there is provided an aqueous acid nickel electroplating bath comprising an aqueous solution of a nickel salt, said solution maintained at a pH in the range of about 3 to 5 and having dissolved therein as primary brightener in an effective amount, an acrylate selected from the group consisting of

(1) an acrylic monomer of the formula:

\[ CH=C=O-\underset{R}{\overset{O}{\longrightarrow}}-O-C_{n}H_{2n}N(R')=X^- \]

wherein

- \( R \) is methyl or hydrogen,
- \( n \) is a positive whole integer of 1 to 3 inclusive,
- \( R' \) is alkyd of 1 to 4 carbon atoms,
- \( R'' \) is alkyd of 1 to 4 carbon atoms,

\[ -CH_2=CH-COOCH_3 \]
\[ -CH_2=CH-COOCH_3 \]
\[ -CH_2=CH-COOCH_3 \]
\[ -CH_2=CH-COOCH_3 \]
\[ -CH_2=CH-COOCH_3 \]
\[ -CH_2=CH-COOCH_3 \]

(2) a homopolymer of said acrylic monomer, and
(3) a copolymer of said acrylic monomer with at least one ethylenically unsaturated monomer selected from the group consisting of an \( \alpha,\beta \)-ethylenically unsaturated monomeric acid, an alkyl ester of said acid wherein the alkyl group is from 1 to 4 carbon atoms, acrylonitrile, acrylamide, methacrylamide, vinyl acetate, vinyl sulfone and vinyl pyridine, the molar ratio of said acrylic monomer to said unsaturated monomer being within the range of 0.9:0.1 to 0.1:0.9.
(2) a homopolymer of said acrylate monomers, and
(3) a copolymer of said acrylate monomer with at least one ethynylunaturated monomer selected from the group consisting of an α,β-ethylenically unsaturated monomer, an alkyl ester of said acid wherein the alkyl group is from 1 to 4 carbon atoms, acrylonitrile, acrylamide, methacrylamide, vinyl acetate, vinyl sulfone and vinyl pyridine, the molar ratio of said acrylate monomer to said unsaturated monomer being within the range of 0.9:0.1 to 0.1:0.9.

There is also provided a process of electroplating bright nickel from the aforesaid electroplating bath.

**DETAILED DESCRIPTION OF THE INVENTION**

Generally, the invention pertains to the electro-deposition of nickel from aqueous, acidic nickel electroplating baths known to those skilled in the art. These baths are usually formed by the dissolution of at least one nickel salt in an aqueous, acid solution. Conventional baths and processes for electroplating bright nickel are described in "Principles of Electroplating and Electroforming," Blum and Hogaboom, pages 362-381, revised third edition, 1949, McGraw-Hill, Inc., New York; and in "Modern Electroplating," edited by A. G. Gray, The Electrochemical Society, 1953, pages 299-355. Operating conditions disclosed, including pH, temperature, current density and the concentration of bath ingredients are applicable to the present invention. Generally, the pH will be in the range of 3 to 5 and usually 3.5 to 4.5, while the temperature will be in the range of 40 to 70°C. and usually 55 to 65°C. Practically all baths for electroplating bright nickel contain nickel sulfate; a chloride, usually nickel chloride; a buffering agent, usually borax; and optionally a wetting agent. Such baths include the well-known Watts bath and the high chloride bath. Other baths may contain, as the source of nickel, a combination of nickel fluoroborate with nickel sulfate and nickel chloride, or a combination of nickel fluoroborate with nickel chloride. Typical Watts baths and high chloride baths are as follows:

**Watts baths**

<table>
<thead>
<tr>
<th>Component</th>
<th>g/L</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfate</td>
<td>200-400</td>
<td></td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>30-75</td>
<td></td>
</tr>
<tr>
<td>Boric acid</td>
<td>30-50</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>55-65</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>3-5</td>
<td></td>
</tr>
</tbody>
</table>

**High chloride baths**

<table>
<thead>
<tr>
<th>Component</th>
<th>g/L</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel chloride</td>
<td>150-300</td>
<td></td>
</tr>
<tr>
<td>Nickel sulfate</td>
<td>40-150</td>
<td></td>
</tr>
<tr>
<td>Boric acid</td>
<td>30-50</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>55-65</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>3-5</td>
<td></td>
</tr>
</tbody>
</table>

The primary brighteners of the present invention may be used in concentrations ranging between about 0.001 to 5 g/L, preferably between about 0.002 to 2 g/L, the particular concentration used depending on the type and concentration of the secondary and secondary auxiliary brighteners used. Other factors to be considered are concentrations of the bath ingredients, the operating conditions and the degree and rate of brightening and leveling desired.

The primary brighteners of this invention are certain quaternized dialkylaminoalkylacylamines and more particularly homopolymers of these monomers or copolymers of these monomers with other ethynylunaturated monomers. The quaternized dialkylaminoalkylacylamines used in this invention have the general formula:

\[
\begin{align*}
\text{CH}_3 & - \text{C} - \text{O} - \text{C} - \text{C}_2\text{H}_5 - \text{N} \left( \text{R'} \right) \text{R} \text{R} \text{X} \\
\end{align*}
\]

wherein

- R is methyl or hydrogen,
- n is a positive whole integer of 1 to 3 inclusive,
- R' is alkyl of 1 to 4 carbon atoms,
- R'' is alkyl of 1 to 4 carbon atoms, \( \text{-CH}_2\text{CH} = \text{CH}_2 \), \( \text{-CH}_2\text{C} = \text{C} \text{H} \), \( \text{-CH}_2\text{COOCH}_3 \), \( \text{-CH}_2\text{COOC}_2\text{H}_5 \), \( \text{-CH}_2\text{COR} \) where R is as defined above,
- \( \text{-CH}_2\text{CONH}_2 \),
- \( \text{-CH}_2\text{CN}, \text{-CH}_2\text{CH}_2\text{OH}, \text{-CH}_2\text{CH}_2\text{COO}^- \) or \( \text{-CH}_2\text{CH}_2\text{CH}_2\text{SO}_4^- \), and
- X' is \( \text{CH}_3\text{SO}_4^- \), \( \text{C}_2\text{H}_5\text{SO}_4^- \), halide or is absent when \( R'' = \text{-CH}_2\text{COO}^- \) or \( \text{-CH}_2\text{CH}_2\text{CH}_2\text{SO}_4^- \);

(2) a homopolymer of said acrylate monomer, and
(3) a copolymer of said acrylate monomer with at least one ethynylunaturated monomer selected from the group consisting of an α,β-ethylenically unsaturated monomer, and alkyl ester of said acid wherein the alkyl group is from 1 to 4 carbon atoms, acrylonitrile, acrylamide, methacrylamide, vinyl acetate, vinyl sulfone and vinyl pyridine, the molar ratio of said acrylate monomer to said unsaturated monomer being within the range of 0.9:0.1 to 0.1:0.9.

One monomer falling under this general description which has been found to be particularly useful as a primary brightener is: 2-methacryloxyethyl, dimethyl propargyl ammonium bromide

\[
\text{CH}_3 = \text{C} = \text{C} = \text{O} - \text{C} = \text{O} - \text{C} = \text{C} \text{H}_2 \text{N} \left( \text{CH}_2 \right)_2 \text{CH} = \text{CH}_2 - \text{CH}_2\text{CH} = \text{CH}_2 \text{Br} -
\]

which may be prepared by the addition of propargyl bromide to dimethylaminomethyl methacrylate in a suitable solvent.

This monomer may be readily polymerized in aqueous solution under the action of a peroxide initiator and a temperature of 60 to 80°C. to give a homopolymer which shows enhanced brightening-leveling characteristics over the monomer but which also inhibits plating at low current densities, i.e., less than 10 amperes/f帛t².

The problem of low current density skipping, while retaining brightening-leveling characteristics, is overcome by copolymerizing the quaternized dialkylaminoalkylacylamides with at least one other ethynylunaturated monomer such as an α,β-ethylenically unsaturated monomer such as acrylonitrile or methacrylic acid, an alkyl ester of said acid wherein the alkyl group is from 1 to 4 carbon atoms, methacrylamide, acrylamide, acrylonitrile, vinyl acetate, vinyl sulfone and vinyl pyridine. The molar ratios of the acrylamide to the other monomer can vary between about 0.9:0.1 to 0.1:0.9. Of particular interest in this capacity is the copolymer formed between: 2-methacryloxyethyl trimethyl ammonium methyl sulfate and methacrylic acid

\[
\begin{align*}
\text{CH}_3 & - \text{C} - \text{O} - \text{C} - \text{C}_2\text{H}_5 - \text{N} \left( \text{CH}_2 \right)_2 \text{CH} = \text{CH}_2
\end{align*}
\]

The above copolymer is preferably used with molar ratios of n/m varying between 0.7 and 0.3, although maximum benefits are obtained at ratios of n/m about 0.7/0.3.

Many primary brightener equivalents will be readily apparent to one skilled in the art. Thus, some benefits would be expected for the copolymers of the quaternized dialkylaminoalkylacylamides with any other homopolymerizable ethynylunaturated monomer. Further, the invention includes terpolymers, tetrapolymers and other copolymers.

Secondary brighteners, usually used at a concentration of 1 to 20 g/L, may consist typically of aromatic sulfonates, sulfonamides or sulfamates such as sodium or potassium salts of saccharin, 1,3,5-naphthalene trisulfonate p-toluene sulfonamide, benzene sulfonic acid (usually in form of sodium or potassium salt). The sec-
ordinary brighteners are generally characterized by having at least one sulfone or sulfonic acid group attached to a nuclear carbon of a homocyclic aromatic ring. These materials have a brightening effect on the nickel deposits but, more importantly, impart ductility. In addition, other sulfonated unsaturated hydrocarbons, such as sodium allyl sulfonate and sodium-3-chloro-2-buten-1-sulfone may be added to the bath as auxiliary secondary brighteners to further improve the brightness range and ductility of the nickel deposits. Auxiliary secondary brighteners as well as the secondary brighteners are well-known to those skilled in the art.

The invention can be further understood by referring to the following examples in which parts and percentages are by weight unless otherwise indicated. In each of the examples, an aqueous, acid nickel bath of the following composition was used as the base solution:

<table>
<thead>
<tr>
<th>G. L.</th>
<th>Nickel sulfate</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nickel chloride</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Boric acid</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Saccharin</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Sodium allyl sulfonate</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>2</td>
</tr>
</tbody>
</table>

Additives were added to this base bath in 267 ml. Hull Cell tests. The tests were conducted at 60-65° C., using steel panels, and electroplating was at 2-amps for 10 minutes. Agitation of the bath was accomplished by a mechanical stirrer sweeping parallel to the panels. Prior to plating, each panel was anodically cleaned, scratched lengthwise with one pass of 240 grit emery cloth to effect a visual comparison of leveling to be made, and again anodically cleaned.

**EXAMPLE 1**

2-methacryloxyethyl, propargyl, dimethyl ammonium bromide (A) was prepared by adding 8 g. propargyl bromide to 12 g. dimethylaminomethacrylate in 20 g. methyl ethyl ketone. The white crystals analyzed as C: 47.88%, H: 6.58%, N: 5.13%. Theory C: 47.85%, H: 6.52%, N: 5.07%. Theory for Cl: 14.18%. In a Hull Cell test using (A) in an amount of 0.04 g./l. of plating bath, the panel showed a bright nickel deposit above about 10 a./ft.². The degree of leveling was excellent, i.e., virtually all of the scratch marks were completely covered.

**EXAMPLE 2**

2-methacryloxyethyl, carb oxamidomethyl, dimethyl ammonium chloride (B) was prepared by standing together 9.4 g. of chloroacetamide and 8 g. dimethylaminomethacrylate in 25 g. dimethylformamide for 12 days. After this time, a few white solids had appeared. On pouring the solution into methyl ethyl ketone, considerable white crystalline solids precipitated. They contained Cl: 13.92%. Theory for Cl: 14.18%. In a Hull Cell test using (B) in an amount of 0.16 g./l. of plating bath, the panel showed very bright nickel above about 12 a./ft.². The degree of leveling was good, i.e., most of the scratch lines were covered.

**EXAMPLES 3-5**

In Table I are listed other quaternized dimethylaminomethacrylates which were prepared by adding on ap-

### TABLE I—QUATERNIZED DIMETHYLAMINOMETHACRYLATES

<table>
<thead>
<tr>
<th>Example</th>
<th>Monomer</th>
<th>Found, percent</th>
<th>Theor. percent</th>
<th>Amount used, g./l.</th>
<th>Bright level range, A.F.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>C</td>
<td>62.79 7.69 5.27 49.82 7.58 5.26</td>
<td>62 7.6 5.2 49.8 7.6 5.2</td>
<td>0.04</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>D</td>
<td>51.55 7.34 12.12 51.75 7.34 12.07</td>
<td>51.5 7.3 12.1 51.7 7.3 12.0</td>
<td>0.02</td>
<td>&gt;1</td>
</tr>
<tr>
<td>6</td>
<td>E</td>
<td>65.8 7.61 4.99 47.3 7.52 4.0</td>
<td>65.8 7.6 5.0 47.3 7.5 4.0</td>
<td>0.06</td>
<td>&gt;4</td>
</tr>
</tbody>
</table>

- C = 2-methacryloxyethyl, carb oxamidomethyl, dimethyl ammonium chloride
- D = 2-methacryloxyethyl, carb oxamidomethyl, dimethyl ammonium chloride
- E = 2-methacryloxyethyl, dimethyl, 3-sulfopropyl ammonium betaine

**EXAMPLE 6**

2-methacryloxyethyl, dimethyl, allyl ammonium bromide (F) was prepared by adding 12 g. allyl bromide to 8 g. dimethylaminomethacrylate in 25 g. methyl ethyl ketone. The white crystals were found to contain 29.0% Br. Theory 28.8%. Used in amounts of 0.02-0.16 g./l. of plating bath. (F) was found to have only marginal action as a brightener-leveler. Consequently, (F) was polymerized by warming together 5 g. (F), 25 g. water, 0.05 g. potassium persulfate in a stirred vessel at 80° C. for 1 hour. Poly (F) was precipitated as a white rubbery material on pouring into acetone. After drying at 60° C. under vacuum, brownish brittle solids, easily soluble in water, were obtained.

In a Hull Cell plating test, using poly (F) in an amount of 0.04 g./l. of plating bath, poly (F) was found to be an excellent brightener-leveler above 40 a./ft.². The nickel deposit was mirror bright with all scratches completely leveled. Lesser amounts of poly (F) in the plating bath permitted nickel deposition below 40 a./ft.², but with some loss of leveling ability. Thus, at 0.008 g./l., bright nickel was obtained above 1 a./ft.², but only slight leveling was observed.

**EXAMPLES 7-12**

In Table II are listed other homopolymers prepared in a manner similar to that of Example 6 and found to have brightening-leveling action when added to the nickel bath in amounts of 0.008 g./l. to 0.04 g./l.

### TABLE II—HOMOPOLYMERS OF QUATERNIZED DIMETHYLAMINOMETHACRYLATES

<table>
<thead>
<tr>
<th>Example</th>
<th>Poly (2-methacryloxyethyl, dimethyl, propargyl ammonium bromide)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Poly (2-methacryloxyethyl, dimethyl, propargyl ammonium bromide)</td>
</tr>
<tr>
<td>8</td>
<td>Poly (2-methacryloxyethyl, dimethyl, carboxymethyl ammonium chloride)</td>
</tr>
<tr>
<td>9</td>
<td>Poly (2-methacryloxyethyl, dimethyl, carb oxamidomethyl ammonium chloride)</td>
</tr>
<tr>
<td>10</td>
<td>Poly (2-methacryloxyethyl, dimethyl, 3-sulfopropyl ammonium betaine)</td>
</tr>
<tr>
<td>11</td>
<td>Poly (2-methacryloxyethyl, dimethyl, 3-sulfopropyl betaine)</td>
</tr>
<tr>
<td>12</td>
<td>Poly (2-methacryloxyethyl, diethyl, propargyl ammonium bromide)</td>
</tr>
</tbody>
</table>

**EXAMPLES 13-18**

A series of copolymers of 2-methacryloxyethyl trimethyl ammonium methyl sulfate (M) with methacrylic acid (N) in mol. ratios of M/N varying between 0.9/0.1 and 0.1/0.9 were prepared by polymerizing the monomers together in aqueous solution, using potassium persulfate as catalyst. Reaction conditions were total monomers 0.1 mole; concentration in aqueous solution, 20-30% by weight; potassium persulfate 0.02 to 0.04 g.; temperature, 80° C.; time, 20-60 minutes. The polymers were precipitated in acetone and dried under vacuum at 60° C. to give brittle, colorless solids easily soluble in water. Composition was found by microanalysis and is shown in Table III together with plating performance.
TABLE III—2-METHACRYLOYXETHYL TRIMETHYL AMMONIUM METHYL-SULFATE (M) — METHACRYLIC ACID (N) COPOLYMERS

<table>
<thead>
<tr>
<th>Example number</th>
<th>M</th>
<th>N</th>
<th>Found percent</th>
<th>Amount, g/l</th>
<th>Bright range, A/L</th>
<th>Leveling</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>0.10</td>
<td>0.00</td>
<td>0.03</td>
<td>0.50</td>
<td>&gt;2 G-E</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>0.10</td>
<td>0.00</td>
<td>0.03</td>
<td>0.50</td>
<td>&gt;2 G-E</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.06</td>
<td>0.00</td>
<td>0.03</td>
<td>0.50</td>
<td>&gt;2 G-E</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>0.06</td>
<td>0.00</td>
<td>0.03</td>
<td>0.50</td>
<td>&gt;2 G-E</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>0.06</td>
<td>0.00</td>
<td>0.03</td>
<td>0.50</td>
<td>&gt;2 G-E</td>
<td></td>
</tr>
</tbody>
</table>

Note—L.V. = Intrinsic Viscosity (by flow viscometer); levelling, S = slight, few scratches covered; F = fair; G = good, most scratches covered; E = excellent, virtually all scratches covered.

EXEMPLARY 19–23

In this set of examples a series of copolymers between quaternized dialkylaminoethylacrylates (X) and other ethylenically unsaturated monomers (Y) were prepared by copolymerization in aqueous solution under the action of a peroxide initiator using conditions similar to those in Examples 13 to 18. The polymers were then precipitated in acetone and again evaluated as in previous examples. Composition and plating performance are shown in Table IV.

TABLE IV—QUATERNIZED DIALKYLAMINOETHYLACRYLATE (X)—VINYL (Y) COPOLYMERS

<table>
<thead>
<tr>
<th>Example</th>
<th>X</th>
<th>Y</th>
<th>Molar ratio, X/Y</th>
<th>Amount, g/l</th>
<th>Bright range, A/L</th>
<th>Leveling</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>2-methacryloyxethyl trimethyl ammonium methyl sulfonate</td>
<td>0.5/0.5</td>
<td>0.02</td>
<td>&gt;4 F-G</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>2-dodecyl trimethyl ammonium methyl sulfonate</td>
<td>0.5/0.5</td>
<td>0.02</td>
<td>&gt;4 G-E</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Methacrylamide</td>
<td>0.5/0.5</td>
<td>0.02</td>
<td>&gt;4 E</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Acrylonitrile</td>
<td>0.5/0.5</td>
<td>0.02</td>
<td>&gt;4 G</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Acrylamide</td>
<td>0.5/0.5</td>
<td>0.02</td>
<td>&gt;4 G</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

What is claimed is:

1. An aqueous acid nickel electropolishing bath comprising an aqueous solution of a nickel salt, said solution maintained at a pH in the range of about 3 to 5 and having dissolved therein as primary brightener an effective amount of an acrylic acid selected from the group consisting of

(1) an acrylic acid monomer of the formula:

\[
\text{CH}_2\text{C} = \text{C} - \text{C} - \text{O} - \text{C}_2\text{H}_3\text{N}^+\text{(R')_2R''X^-}
\]

wherein

- R is methyl or hydrogen,
- n is a positive whole integer of 1 to 3 inclusive,
- R' is alkyl of 1 to 4 carbon atoms,
- R'' is alkyl of 1 to 4 carbon atoms,

(2) a homopolymer of said acrylic acid monomer, and

(3) a copolymer of said acrylic acid monomer with at least one ethylenically unsaturated monomer selected from the group consisting of an α, β-ethylenically unsaturated monocarboxylic acid, an alkyl ester of said acid wherein the alkyl group is from 1 to 4 carbon atoms, acrylonitrile, acrylamide, methacrylamide, vinyl acetate, vinyl sulfone and vinyl pyridine, the molar ratio of said acrylic monomer to said unsaturated monomer being within the range of 0.9:0.1 to 0.1:0.9.

2. The acid electropolishing bath of claim 1 wherein the acrylic acid is a copolymer of an acrylate monomer of the general formula:

\[
\text{CH}_2\text{C} = \text{C} - \text{C} - \text{O} - \text{C}_2\text{H}_3\text{N}^+\text{(R')_2R''X^-}
\]

wherein

- R is methyl or hydrogen,
- R' is methyl or ethyl,
- R'' is alkyl of 1 to 4 carbon atoms,

3. The acid electropolishing bath of claim 2 wherein the pH of the bath is within the range of about 3.5 to 4.5 and the copolymer concentration is about 0.001 to 5 g/l.

4. The acid electropolishing bath of claim 3 wherein the copolymer concentration is about 0.002 to 2 g/l.

5. The acid electropolishing bath of claim 2 wherein the ethylenically unsaturated monomer is methacrylic acid.

6. The acid electropolishing bath of claim 2 wherein the copolymer is about 70 molar percent of 2-methacryloyloxyethyl trimethyl ammonium methyl sulfonate and about 30 molar percent of methacrylic acid.

7. The acid electropolishing bath of claim 1 wherein the acrylic acid is an acrylate monomer of the general formula:

\[
\text{CH}_2\text{C} = \text{C} - \text{C} - \text{O} - \text{C}_2\text{H}_3\text{N}^+\text{(R')_2R''X^-}
\]
wherein

R is methyl or hydrogen,

R’ is methyl or ethyl,

R” is alkyl of 1 to 4 carbon atoms,

-CH₂CH=CH₂, -CH₂=CH₂, -CH₂COOCH₂⁻,

-CH₂COOCH₂⁻, -CH₂COR where R is as defined above,

-CH₂CONH₂, -CH₂CN, -CH₂CH₂OH

-CH₂CH₂COO⁻ or -CH₂CH₂CH₂SO₄⁻, and

X⁻ is CH₃SO₄⁻, C₂H₅SO₄⁻, halide or is absent when R” is -CH₂CH₂COO⁻ or -CH₂CH₂CH₂SO₄⁻.

8. The acid electropolytating bath of claim 7 wherein the acrylate monomer is 2-methacyloxyethyl, dimethyl propargyl ammonium bromide or 2-acryloyxethyl, diethyl propargyl ammonium bromide.

9. The acid electropolytating bath of claim 7 wherein the pH of the bath is within the range of about 3.5 to 4.5 and the acrylate monomer concentration is about 0.001 to 5 g/L.

10. The acid electropolytating bath of claim 1 wherein the acrylate is a homopolymer of an acrylate monomer of the general formula:

\[ CH₃-C≡C-OH₂N⁺(R’)R''⁻X⁻ \]

wherein

R is methyl or hydrogen,

R’ is methyl or ethyl,

R” is alkyl of 1 to 4 carbon atoms, -CH₂CH=CH₂, -CH₂=C=CH₂, -CH₂COOCH₂⁻,

-CH₂COOCH₂⁻, -CH₂COR where R is as defined above,

-CH₂CONH₂, -CH₂CN, -CH₂CH₂OH

-CH₂CH₂COO⁻ or -CH₂CH₂CH₂SO₄⁻, and X⁻ is CH₃SO₄⁻, C₂H₅SO₄⁻, halide or is absent when R” is -CH₂CH₂COO⁻ or -CH₂CH₂CH₂SO₄⁻.

11. The acid electropolytating bath of claim 10 wherein the pH of the bath is within the range of about 3.5 to 4.5 and the acrylate homopolymer concentration is about 0.001 to 5 g/L.

12. The acid electropolytating bath of claim 1 wherein the acrylate is added to give a bath concentration within the range of about 0.001 to 5 g/L.

13. In a process of electropolytating nickel from an aqueous acid nickel electropolytating bath having a nickel salt dissolved therein the improvement comprising: maintaining said bath at a pH in the range of about 3 to 5 and adding thereto as a primary brightener an effective amount of an acrylate selected from the group consisting of:

(1) an acrylate monomer of the formula:

\[ CH₃-C≡C-OH₂N⁺(R’)R''⁻X⁻ \]

wherein

R is methyl or hydrogen,

n is a positive whole integer of 1 to 3 inclusive,

R’ is alkyl of 1 to 4 carbon atoms,

R” is alkyl of 1 to 4 carbon atoms, -CH₂CH=CH₂, -CH₂=C=CH₂, -CH₂COOCH₂⁻,

-CH₂COOCH₂⁻, -CH₂COR where R is as defined above, -CH₂CONH₂, -CH₂CN, -CH₂CH₂OH

-CH₂CH₂COO⁻ or -CH₂CH₂CH₂SO₄⁻, and

X⁻ is CH₃SO₄⁻, C₂H₅SO₄⁻, halide or is absent when R” is -CH₂CH₂COO⁻ or -CH₂CH₂CH₂SO₄⁻.

(2) a homopolymer of said acrylate monomer and

(3) a copolymer of said acrylate monomer with at least one ethylenically unsaturated monomer selected from the group consisting of an α, β-ethylenically unsaturated monomonoxylic acid, an alkyl ester of said acid wherein the alkyl group is from 1 to 4 carbon atoms, acrylonitrile, acrylamide, methacrylamide, vinyl acetate, vinyl sulfone and vinyl pyrindine, the molar ratio of said acrylate monomer to said unsaturated monomer being in the range of 0.9:0.1 to 1:0.9.

14. The process of claim 20 wherein the acrylate is added to give a bath concentration of about 0.002 to 2 g/L, the pH is maintained within the range of about 3.5 to 4.5 and the bath is at a temperature in the range of about 40 to 70°C.

15. The process of claim 14 wherein the acrylate is a copolymer of an acrylate monomer of the general formula:

\[ CH₃-C≡C-OH₂N⁺(R’)R''⁻X⁻ \]

wherein

R is methyl or hydrogen,

R’ is methyl or ethyl,

R” is alkyl of 1 to 4 carbon atoms, -CH₂CH=CH₂, -CH₂=C=CH₂, -CH₂COOCH₂⁻,

-CH₂COR where R is as defined above, -CH₂CONH₂, -CH₂CN, -CH₂CH₂OH

-CH₂CH₂COO⁻ or -CH₂CH₂CH₂SO₄⁻, and X⁻ is CH₃SO₄⁻, C₂H₅SO₄⁻, halide or is absent when R” is -CH₂CH₂COO⁻ or -CH₂CH₂CH₂SO₄⁻, with at least one ethylenically unsaturated monomer selected from the group consisting of an α, β-ethylenically unsaturated monomonoxylic acid, an alkyl ester of said acid wherein the alkyl group is from 1 to 4 carbon atoms, acrylonitrile, acrylamide, methacrylamide, vinyl acetate, vinyl sulfone and vinyl pyrindine, the copolymer having a molar ratio of said acrylate monomer to said unsaturated monomer within the range of 0.7/0.3 to 0.3/0.7 and the bath is at a temperature in the range of about 20 to 30°C.

16. The process of claim 15 wherein the ethylenically unsaturated monomer is methacrylic acid.

17. The process of claim 15 wherein the copolymer is about 70 molar percent of 2-methacyloxyethyl, trimethyl ammonium methyl sulfinate and about 30 molar percent of methacrylic acid.

18. The process of claim 14 wherein the acrylate is an acrylate monomer of the formula:

\[ CH₃-C≡C-OH₂N⁺(R’)R''⁻X⁻ \]

wherein

R is methyl or hydrogen,

R’ is methyl or ethyl,

R” is alkyl of 1 to 4 carbon atoms, -CH₂CH=CH₂, -CH₂=C=CH₂, -CH₂COOCH₂⁻,

-CH₂COR where R is as defined above, -CH₂CONH₂, -CH₂CN, -CH₂CH₂OH, -CH₂CH₂COO⁻ or

-CH₂CH₂CH₂SO₄⁻, and

X⁻ is CH₃SO₄⁻, C₂H₅SO₄⁻, halide or is absent when R” is -CH₂CH₂COO⁻ or -CH₂CH₂CH₂SO₄⁻.

19. The process of claim 14 wherein the acrylate is a homopolymer of an acrylate monomer of the general formula:
wherein
R is methyl or hydrogen,
R' is methyl or ethyl,
R'' is alkyl of 1 to 4 carbon atoms, —CH₂CH=CH₂,
—CH₂C≡CH, —CH₂COOCH₃, —CH₂COOC₂H₅,
—CH₂COR where R is as defined above,
—CH₂CONH₂, —CH₂CN, —CH₂CH₂OH,
—CH₂CH₂COO⁻ or —CH₂CH₂CH₂SO₃⁻, and X⁻ is
CH₃SO₄⁻, C₂H₅SO₄⁻, halide or is absent when R'' is
—CH₂CH₂COO⁻ or —CH₂CH₂CH₂SO₃⁻.

20. The process of claim 13 wherein the acrylate is added to give a bath concentration within the range of about 0.001 to 5 g./l.

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