Compositions of the type set forth herein have been found to produce leveling when employed with an aqueous acid solution of nickel material capable of supplying nickel ions such as, for instance, the familiar all chloride, all sulfate, sulfate-chloride or Watt's type, nickel fluoroborate, nickel sulfamate types and combinations thereof. In general, leaver compounds of the aforementioned type may be present in a plating bath in a range from .005 g./l. to 1.0 g./l. Within this broad concentration range there are three more limited ranges wherein the limits are determined by the type of cooperating additives employed with the leaver and by the type of nickel coating employed. When the leaver compound is employed alone in a nickel plating bath without the use of cooperating compounds, the leaver is preferably present in the range of from .005 g./l. to 0.1 g./l. When the leaver compound is employed in a nickel plating bath containing cooperating compounds for purposes of obtaining a semi-bright nickel plate, the leaver is preferably present in the range of from .01 g./l. to 0.3 g./l. When the leaver compound is employed in a nickel plating bath containing cooperating compounds for purposes of obtaining a bright nickel plate, the leaver is preferably present in the range of from .05 g./l. to 1.0 g./l. Preferred concentration ranges for certain specific leaver compounds are given in the following table designated as Table I.

**TABLE I**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Semi-bright level or cooperating compound, g./l.</th>
<th>Bright level or cooperating compound, g./l.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-[B-oxypyridine-1-carboxamido]pyrrole-1,4-dicarboxamide</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>4,5,6-tri-oxa-1,5-diepyridine-2,3-dicarboxamide</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>1,4-bis[5-amino-1-hydroxy-carboxamide]butane-2</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>1,4-bis[3-oxo-3-methyl-1-proline-carboxamide]butane-2</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>1,4-bis(oxocardamido)butane-2</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>1,4-bis(oxocardamido)butane-2</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
</tbody>
</table>

In increased leveling and more uniform lustre are obtained with the leaver compounds of this invention when they are employed in combination with a second cooperating compound. The cooperating compound is defined as a tri-halo aldehyde, or acetals or hemiacetals of such aldehydes. Specific examples of such compounds are given in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Semi-bright level or cooperating compound, g./l.</th>
<th>Bright level or cooperating compound, g./l.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1-diethoxy-2,2,2-trichloroethane</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>1,1-dimethoxy-2,2,2-trichloroethane</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>1,1-dimethoxy-2,2,2-trichloroethane</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>1,1-dimethoxy-2,2,2-trichloroethane</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>1,1-dimethoxy-2,2,2-trichloroethane</td>
<td>0.05-0.10</td>
<td>0.05-0.10</td>
</tr>
</tbody>
</table>

In general, the compounds of Table II when present in semi-bright plating solutions are employed in concen-
the preferred cooperating addition agent is trichloroethanal, which is present in the semi-bright plating solution in concentration of 0.1 to 0.5 gram per liter, and preferably from 0.3 to 0.1 gram per liter.

Constituents of the plating solution according to the preferred practice of this invention are:

(1) Water
(2) A source of nickel ions selected from the group consisting of:
   Nickel sulfate
   Nickel chloride
   Nickel sulfamate
   Nickel fluoborate and combinations thereof
(3) A leveling agent selected from the group of Table I.
(4) A cooperating compound selected from the group of Table II (optional).
(5) A wetting agent (optional).

An additional ingredient of the solution which is desirable is a buffering agent such as boric acid, formic acid, sodium formate and the like.

It will be noted that in reference to the major constituent of the plating solution the solutions are similar to the well-known all chloride, all sulfate, sulfate-chloride or Watts-type nickel sulfamate and nickel fluoborate plating solution and combinations thereof. The essential feature of the invention is the use of an acid nickel plating solution having one or more nickel electrolytes and additionally containing one or more cooperating additivies, at least one of which is the novel leveling compound of this invention and preferably a cooperating addition agent selected from the compounds of Table II.

In the preparation of the plating solution according to the invention, we add to each of the basic nickel containing solutions a suitable quantity of the leveling compound and preferably one or more of the cooperating compounds. The plating solution for consistent results contains an antising agent, although the deposits may be suitable without the antising agent. Sodium lauryl sulfate or other wetting agents such as the sodium sulfate derivative of 7-ethyl-2-methyl-undecanol-4 and the dihexyl ester of sodium sulfo-cetic acid may be used as an antising agent, although its use is not essential and other mixtures or admixtures of wetting agents may be used to control the pitting.

Specific examples of the electroplating solutions containing different cooperating additives are illustrated in the following table, which has been designated as Table III. It should be understood that the specific electroplating solutions may be employed with or without air agitation.

### Table III

<table>
<thead>
<tr>
<th>Solution</th>
<th>NISO&lt;sub&gt;4&lt;/sub&gt;6H&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>ozs./gal.</th>
<th>NiCl&lt;sub&gt;2&lt;/sub&gt;6H&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>ozs./gal.</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;BO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>ozs./gal.</th>
<th>pH</th>
<th>Temperature °F</th>
<th>Current density as.f.</th>
<th>to which is added:</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>40</td>
<td></td>
<td>6</td>
<td></td>
<td>4.5</td>
<td></td>
<td></td>
<td>140</td>
<td>45</td>
<td>HC=C—CH&lt;sub&gt;2&lt;/sub&gt;OCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CONH&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>[2]</td>
<td>45</td>
<td></td>
<td>4</td>
<td></td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Trichloroethanal</td>
</tr>
<tr>
<td>[3]</td>
<td>70</td>
<td></td>
<td>0.1</td>
<td></td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[4]</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[5]</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[6]</td>
<td>0.07</td>
<td></td>
<td>0.1</td>
<td></td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The basic nickel solution of Example 1 to which is added:

- HC=C—CH<sub>2</sub>—O(CH<sub>3</sub>)<sub>2</sub>—CONH<sub>2</sub> g./l—0.03
- Tribrromoethanal g./l—0.3

While the foregoing specific electroplating baths are prepared in concentrations and employed at current densities such as will result in the deposition of a semi-bright nickel plate, it should be understood that bright nickel deposits may be obtained by employing appropriate concentrations and current densities. In brief, when a bright nickel deposit is desired, the leveling addition agent should be employed in concentrations from 0.3 gram per liter to 1.0 gram per liter, while the cooperating addition compound selected from the group consisting of 1,1-dithioxy-2,2,2-trichloroethane, 1-hydroxy-1-ethoxy-2,2,2-trichloroethane, 1,1-dimethoxy-2,2,2-trichloroethane, 1-hydroxy-1-methoxy-2,2,2-trichloroethane, trichloroethanal and tribromothanal should be employed in concentrations from 0.5 gram per liter to 0.3 gram per liter.

The leveling addition agent of this invention has been found to be suitable for electrodepositing nickel upon any of the basis metals commonly employed in the electroplating art, such as, for instance, iron, steel, copper, brass and zinc. It has been found, however, that the leveling addition agent of this invention and particularly when the leveling addition agent of this invention is employed in conjunction with the cooperating addition agent that enhanced nickel electrodeposits are obtained on zinc die castings. The zinc basis metal is, of course, subjected to those pretreatment operations common to the art of electroplating prior to the deposition of nickel from the nickel plating bath of this invention. The coating of zinc base metal with copper is commonly done prior to electrodeposition of nickel. In general, the degree of leveling obtained through the deposition of a semi-bright plate of this invention is from 20% to 50% for 1 mil deposits. The percentage of leveling is defined as

\[
100 \times \text{decrease in roughness due to plating} \div \text{initial roughness of basis metal}
\]

Having thus disclosed our invention, what we claim is:

1. A nickel plating composition comprising an aqueous acid solution of nickel material supplying nickel ions and a leveling additive having the general formula:

\[
\text{R}_{1}—\text{C} \equiv \text{C}(\text{OH})_{n}—\text{R}_{2}
\]

wherein \( n \) is an integer from 0 to 1 inclusive, \( \text{R}_{1} \) is a member selected from the group consisting of hydrogen
and alkyl having from 1 to 11 carbon atoms, R₂ is a member selected from the group consisting of:

\[(\text{OCH₃CH₂})_n\text{C}⁻\text{NH₂}\]

wherein y is an integer from 1 to 20, w is an integer from 0 to 20, Z is a member selected from the group consisting of hydrogen, alkyl and hydroxymethyl, and R₃ is a member selected from the group consisting of hydrogen, hydroxymethyl, and alkyl group having from 1 to 11 carbon atoms,

\[
\begin{align*}
\text{H} & \quad \text{C}⁻\text{C}⁻\text{R₂} \\
\text{R₁} & \quad \text{H}
\end{align*}
\]

and

\[
\begin{align*}
\text{H} & \quad \text{C}⁻\text{R₂} \\
\text{R₁} & \quad \text{H}
\end{align*}
\]

wherein R₁ and R₂ are the same as previously defined, said leveling additive being present in the range of from .005 gram per liter to 1.0 gram per liter.

2. The nickel plating solution of claim 1 wherein said leveling additive is present in the range of from .005 gram per liter to .1 gram per liter.

3. A nickel plating solution comprising an aqueous acid solution of nickel material supplying nickel ions and a leveling additive having the general formula:

\[
\begin{align*}
\text{R₁} & \quad \text{C}⁻\text{C}⁻\text{R₂} \\
\text{R₄} & \quad \text{H}
\end{align*}
\]

wherein n is an integer from 0 to 1 inclusive, R₁ is a radical selected from the class consisting of hydrogen and an alkyl group having from 1 to 11 carbon atoms, R₂ is a radical selected from the class consisting of:

\[(\text{OCH₃CH₂})_n\text{C}⁻\text{NH₂}\]

and

\[(\text{OCH₃CH₂})_n\text{C}⁻\text{CH}⁻\text{OCH₃CH₂}⁻\text{NH₂}\]

wherein y is an integer from 1 to 20, w is an integer from 0 to 20, Z is a radical of the class consisting of hydrogen, alkyl and hydroxymethyl, and R₃ is selected from the class consisting of hydrogen, hydroxymethyl, alkyl having from 1 to 11 carbon atoms,

\[
\begin{align*}
\text{H} & \quad \text{C}⁻\text{C}⁻\text{R₂} \\
\text{R₁} & \quad \text{H}
\end{align*}
\]

and

\[
\begin{align*}
\text{H} & \quad \text{C}⁻\text{R₂} \\
\text{R₁} & \quad \text{H}
\end{align*}
\]

wherein R₁ and R₂ are the same as previously defined, and at least one cooperating additive selected from the group consisting of:

1,1-diethoxy-2,2,2-trichloroethane,
1-hydroxy-1-ethoxy-2,2,2-trichloroethane,
1,1-dimethoxy-2,2,2-trichloroethane,
1-hydroxy-1-methoxy-2,2,2-trichloroethane,
1-hydroxy-1-ethoxy-2,2,2-tribromoethane,
1,1-dimethoxy-2,2,2-tribromoethane,
trichloroethanol,
tribromoethanol,
and a cooperating additive selected from the group consisting of:

1,1-diethoxy-2,2,2-trichloroethane,
1-hydroxy-1-ethoxy-2,2,2-trichloroethane,
1,1-dimethoxy-2,2,2-trichloroethane,
1-hydroxy-1-methoxy-2,2,2-trichloroethane,
1-hydroxy-1-ethoxy-2,2,2-tribromoethane,
1,1-dimethoxy-2,2,2-tribromoethane,
trichloroethanol,
tribromoethanol,
said leveling agent being present in the range of from .05 gram per liter to 1.0 gram per liter, and said cooperating additive is present in the range of from .05 gram per liter to 0.3 gram per liter.

6. A nickel plating solution comprising an aqueous acid solution of nickel material supplying nickel ions and a leveling additive selected from the group consisting of:

\[
\begin{align*}
\text{HC}⁻\text{C}⁻\text{CH₂CH₂CONH₂} \\
\text{HC}⁻\text{C}⁻\text{CH₂CH₂CONH₂}
\end{align*}
\]

wherein y is an integer from 1 to 20, w is an integer from 0 to 20, Z is a radical selected from the class consisting of hydrogen, alkyl and hydroxymethyl, and R₃ is selected from the class consisting of hydrogen, hydroxymethyl, alkyl having from 1 to 11 carbon atoms,

\[
\begin{align*}
\text{H} & \quad \text{C}⁻\text{C}⁻\text{R₂} \\
\text{R₁} & \quad \text{H}
\end{align*}
\]

and

\[
\begin{align*}
\text{H} & \quad \text{C}⁻\text{R₂} \\
\text{R₁} & \quad \text{H}
\end{align*}
\]

wherein R₁ and R₂ are the same as previously defined, and at least one cooperating additive selected from the group consisting of:

1,1-diethoxy-2,2,2-trichloroethane,
1-hydroxy-1-ethoxy-2,2,2-trichloroethane,
1,1-dimethoxy-2,2,2-trichloroethane,
1-hydroxy-1-methoxy-2,2,2-trichloroethane,
1-hydroxy-1-ethoxy-2,2,2-tribromoethane,
1,1-dimethoxy-2,2,2-tribromoethane,
trichloroethanol,
tribromoethanol,
7droxy-1-ethoxy-2,2,2-trichloroethane, 1,1-dimethoxy-2,2,2-trichloroethane.

81-hydroxy-1-methoxy-2,2,2-trichloroethane, 1-hydroxy-1-ethoxy-2,2,2-tribromoethane, 1,1-dimethoxy-2,2,2-tribromoethane, trichloroethanol, and tribromoethanol, said leveling additive being present in the range of from .01 gram per liter to .3 gram per liter and said cooperating additive being present in the range of from .05 gram per liter to 1.0 gram per liter.

10. The method of claim 9 wherein said cooperating additive is trichloroethanol.

11. The method of claim 9 wherein said leveling additive is present in the range of from .05 gram per liter to 1.0 gram per liter and wherein said cooperating additive is present in the range of from .05 gram per liter to .3 gram per liter.

12. The method of claim 9 wherein said metallic object is a zinc die casting pretreated with a copper coating.

References Cited in the file of this patent

UNITED STATES PATENTS
2,900,707 Brown ----------------- Aug. 25, 1959

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1,234,332 France ------------------ Apr. 11, 1960
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION
Patent No. 3,160,574

December 8, 1964

Jack L. Towle et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 67, for "NH₂COCH₂CH₂OCH₂≡C-CH₂OCH₂CH₂CONH₂"
read -- NH₂COCH₂CH₂OCH₂C≡C-CH₂OCH₂CH₂CONH₂" line 69, for Trichloroethanol" read -- Trichloroethanal --; column 4, line 4, for "NH₂CO(CH₂CH₂O)₃CH₂C≡CCH₂(OCH₂)₃CONH₂" read -- NH₂CO(CH₂CH₂O)₃CH₂C≡CCH₂(OCH₂CH₂)₃CONH₂ --; lines 41 and 42, for "tribromethanal" read -- tribromothanal --; column 5, lines 45 and 46, the formula should appear as shown below instead of as in the patent:

```
CH₃O
```

(OCH₂CH₂)ₙ-OCH₂-CH-C-NHZ

Signed and sealed this 13th day of April 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents