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(54) Title: ELECTROLYTIC PROCESSES WITH REDUCED CELL VOLTAGE AND GAS FORMATION

(57) Abstract: Electrolytic solutions containing organic additive(s) selected from a described class of additives (e.g., 4,6-dihydroxypyrimidine) reduce overall applied electrical potential of electrolytic cells and/or reduce gas formation at the anode(s) or increase copper production rate. Benefits include reducing overall power consumption and reducing acid mist during electrolytic processes.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 02/23052
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**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C25C7/06 C25C1/12 C25C1/16 C25D3/22 C25D1/04  
C25C1/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C25C C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, PAJ, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 1 300 487 A (SHIPLEY CO. L.L.C) 9 April 2003 (2003-04-09) claim 23	1-16
X	EP 0 259 126 A (E.I. DU PONT DE NEMOURS AND COMPANY) 9 March 1988 (1988-03-09) claim 5; examples	1,5-12, 14-16
X	US 4 608 136 A (VAUGHAN, DECEASED ET AL) 26 August 1986 (1986-08-26) column 3, line 55 - column 4, line 33; examples	1,5-12, 14-16
A	US 4 686 017 A (YOUNG ET AL) 11 August 1987 (1987-08-11) column 3, line 55 - column 4, line 33; examples	1-16
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance  
 "E" earlier document but published on or after the international filing date  
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
 "O" document referring to an oral disclosure, use, exhibition or other means  
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
 "&" document member of the same patent family

Date of the actual completion of the international search

22 February 2005

Date of mailing of the international search report

05. 07. 2005

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**INTERNATIONAL SEARCH REPORT**

International Application No  
PCT/US 02/23052

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EL-SUBRUITI G M: "EFFECT OF SOME AMINO COMPOUNDS ON THE ELECTROWINNING OF COPPER"                      U. SCIENTIST PHYL. SCIENCES, XX, XX,                      vol. 7, no. 1, 1995, pages 35-42,                      XP008028287                      page 35 - page 36</p> <p style="text-align: center;">-----</p>	1-16

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 02/23052

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: 4,13,15 (all partially)  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
1, 5-12, 14-16 ( all partially )

**Remark on Protest**

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

## 1. claims: 1,5-12,14-16 (all partially)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of quinhydrone / tetrahydroxy-1,4-quinone hydrate / 3,4-dihydroxa-9,10-diooxo-2-anthracenesulfonic acid, sodium salt monohydrate

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## 2. claims: 1,5-12,14-16 (all partially)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of 1,4-dihydroxybenzene-5-sulfonic acid, potassium salt / 4-toluenesulfonic acid, sodium salt

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## 3. claims: 1-2,5-12,14,16 (all partially)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of 3,5-dimethoxyphenol / 1,3-dihydroxynaphthalene / phloroglucinol dihydrate / 1,3-dihydroxybenzene / 1,3-dihydroxy-5-methoxybenzene / 1,2,4-trihydroxybenzene / 1,2,3-trihydroxybenzene / 1,2-dihydroxybenzene

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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## 4. claims: 1-16 (all partially, except 3 that is complete)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of 4,6-dihydroxy pyrimidine / 2,4,5-trihydroxypyrimidine / 2,4-dihydroxypyrimidine / 4-hydroxypyrimidine / 4,6-dihydroxy-2-methylpirimidine / 2-hydroxypyrimidine hydrochloride / 4,6-diaminopyrimidine

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## 5. claims: 1-2,5-12,14,16 (all partially)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of 3,6-dihydroxypyridazine.

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## 6. claims: 1-2,5-12,14,16 (all partially)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of 4-hydroxypyridine / 2,4 dihydroxypyridine / 2-hydroxypyridine / 3-hydroxydypyridine

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## 7. claims: 1-2,5-12,14,16 (all partially)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of N-hydroxysuccinimide,

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8. claims: 1-2,5-12,14,16 (all partially)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of glycerol.

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9. claims: 1-2,5-12,14,16

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of methanol

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10. claims: 1-2,5-12,14,16 (all partially)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of glucose / sucrose

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11. claims: 1-2,4-16 (all partially)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of 1,4diazabicyclo(2.2.2)octane.

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12. claims: 1-2,4-16 (all partially)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of pyrazine

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13. claims: 1-2,4-16 (all partially)



FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of urea

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14. claims: 1-2,4-16 (all partially)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of 2-amino-2-thiazoline

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15. claims: 1-2,4-16 (all partially)

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of methylsulfoxide.

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16. claims: 1-2,4-16 (all partially)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

An electrolytic process utilizing an electrolytic cell having at least one gasevolving anode, at least one cathode, and an electrolyte solution in contact with said anode and cathode and comprising an acid, a metal ion source and a solvent, said process comprising applying an electrical potential between said anode and said cathode to induce current flow wherein said electrolyte solution contains at least one organic additive in an amount sufficient to reduce cell operating potential at constant current, compared to the same process without such organic additive, said organic additive being selected from the group consisting of L-histidine

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 4,13,15 (all partially)

Present claims 4,13,15 relate to an extremely large number of possible products. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds/products/apparatus/methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the products specifically enumerated in claims 4,13 and 15.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

# INTERNATIONAL SEARCH REPORT

in on patent family members

International:	ication No
PCT/US	02/23052

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