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(54) **Electrodeposition cell.**

(57) An electrodeposition cell has a rotating cathode and a scraper for removing deposit from the cathode. The axial extent of the engaging part of the scraper is less than half (for example 1/63) of the axial extent of the electrode, and that part is axially movable to engage any part of the cathode as the cathode rotates. The scraper does not strip bare the surface of the cathode, but leaves a microscopically rough deposit, which improves the deposition rate.

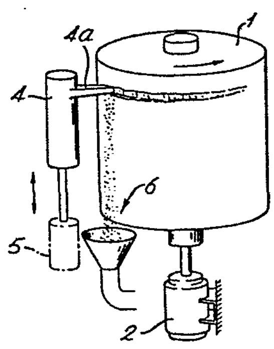

Fig. 1

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ELECTRODEPOSITION CELL

This invention relates to an electrodeposition cell having a rotating cylindrical deposition electrode and to a method of removing deposit from such an electrode.

Rotating cylindrical cathodes for recovering metals from dilute salt solutions in electrodeposition cells are known, for example from UK Patent Specification No. 1505736. Depending on the current density, the peripheral speed of the rotating cylinder, and the salt concentration, the metal may deposit as a loosely adherent deposit which is washed off the cathode. However, the current that can be passed through a freshly washed cathode is much less (e.g. six to sixty times less) than can be passed through a cathode bearing a rough deposit, at comparable current efficiencies.

The invention is an electrodeposition cell having a rotating cylindrical deposition electrode and a means for removing deposit from that electrode, such that the electrode retains a substantially rough electrodeposit (i.e. is not bared). Preferably, this means is a scraper engaging the electrodeposit and breaking away its outer portion. Preferably the axial extent of the engaging part of the scraper does not exceed half the axial extent of the electrode, the engaging part being axially movable so that (with the electrode rotating) the scraper can engage any point on the electrodeposit.

The engaging part may be arranged to be axially movable by making the scraper axially movable, or the scraper may comprise a rotatable helical blade whose axis is parallel to the cylinder axis; rotation of the scraper about its own axis will thus cause the contact area to traverse the electrode axially. Other means of removal to leave a substantially rough surface are possible, such as vibration (which may be ultrasonic) or air-blasting, for example.

The axial extent of the part of the scraper at any instant engaging the electrode preferably does not exceed 0.1 of the axial extent of the electrode, more preferably does not exceed 0.01 thereof, most preferably does not exceed 0.002.

The invention is also a method of removing deposit from a rotating cylindrical deposition electrode in an electrodeposition cell during electrodeposition such that the electrode retains a substantially rough electrodeposit. To keep the electrodeposit at least microscopically rough even the instant after some has been removed, the method of removal may comprise e.g. air-blasting or vibration (which may be ultrasonic), but preferably comprises applying to the electrodeposit, such that it will not bare the electrode, a scraper breaking away the outer portion of the electrodeposit. Preferably the scraper scrapes not more than 0.1 (more preferably not more than 0.01, most preferably not more than 0.002) of the cylindrical area of the electrode in one revolution thereof.

The scraper may comprise a helical blade (as described above) or may comprise a full-axial-extent blade brought into contact with the electrode for only a fraction of a revolution or may comprise a part-axial-extent blade mounted on an axially-moving carrier so that, as the electrode rotates, the scraping follows a helical path (like a screw thread) over the area of the electrode. The carrier may spring back to its starting point after the whole electrode is scraped or may move backwards at the same rate as forwards. The scraper may (unless of full axial extent) contact the electrode continuously, or may contact it intermittently. The degree of contact is such as to scrape off the outer portion only of the deposit.

Although mechanical scraping has clear advantages in reliability, control and simplicity, there are instances when other means of scraping are preferred, e.g. a fluid jet, an air blast or air knife, blasting with glass beads or metal particles (which may be products of the electrodeposition), vibration, or ultrasonics. With the last two, after electrodeposition has been allowed to proceed undisturbed for some time, powder should drop off the electrode, and if the amplitude and frequency are well chosen, the powder rate will equal the electrodeposition rate and the electrode will retain its roughness.

In this way, a continuous stream of deposit can be removed from the electrode and collected from the bottom of the cell, while the electrode remains rough over its area and hence retains a much higher current capacity than if the electrode had been washed or a doctor blade wiped the whole cylindrical surface to bareness every revolution. The roughness is superior to roughening expedients such as knurling the electrode. Indeed, thanks to the permanent high average roughness, mixing in the region immediately around the cylinder approaches theoretically perfect mixing, and therefore the flow-rate through the electrodeposition cell does not affect mass transfer rates to the electrode. Such high yet constant mass transfer is an unusual achievement in chemical reactions. Also, the contact area between the scraper and the electrode is a negligible fraction of the cylindrical area, and hence the scraper physically obstructs electrodeposition but negligibly. The roughness affords a high true surface area on a relatively small-volume electrode.

The invention will now be described by way of example with reference to the accompanying drawings, in which:-

Figure 1 shows a deposition electrode and scraper from a cell according to the invention, and

Figure 2 shows an electrode and alternative scraper from a cell according to the invention.

In Figure 1, a cathode 1 of an electrodeposition cell (which, being otherwise standard, is not further shown or described) is of cylindrical form, diameter 60 mm and height 63 mm, and is driven at 360 revolutions per minute (peripheral velocity: 1.13 m/s) by a motor 2. An upright carrier 4, reciprocated by a pneumatic actuator 5, carries a scraper point 4a made of and contacting the cathode 1 at an area whose height (parallel to the cylinder axis) is 1 mm. It is enlarged on the drawing for clarity.

The cathode 1 is in an aqueous electrolyte of 1.5 M sulphuric acid H_2SO_4 plus 0.014 M copper sulphate $CuSO_4$ at 22C. The Reynolds number at its surface is about 59000.

In use of a brand new hydrodynamically smooth cathode 1, a stop (not shown) holds the scraper point 4a clear of the cathode 1 and a voltage of approximately 2.5V is applied. Current starts to flow at 0.8A, in good accordance with theory, and after about 20 minutes the copper depositing on the cathode begins perceptibly to roughen it. The current starts to rise, after 1 hour reaching 3A (the maximum possible at that current efficiency with a knurled cylinder having a peak-to-valley roughness of 1 mm, according to Kappesser et al, J. Electrochem Soc 118 (1971) p. 1957). Contrary to the Kappesser teaching, however, the current continues to rise, tending to level off at about 6A after 2½ - 3 hours.

The stop is withdrawn, and the scraper point 4a contacts the electrodeposit on the cathode 1. This electrodeposit is rough. Copper powder is scraped off by a dendrite-fracturing action and is collected, as schematically indicated at 6. The actuator 5 pulls the carrier 4 downwards slowly at such a rate (3 mm/minute) that the point 4a leaves a helical trail on the cathode 1, the trail taking about 20 minutes to cover every part of the cylindrical area of the cathode 1. The trail having been formed by a fracturing action, it is rough even when newly formed, and can maintain a current density substantially higher than that predicted by Kappesser, recovering to its maximum after about 1 minute.

Immediately the point 4a has scraped an element of the cathode 1, electrodeposition resumes and the trail eventually disappears (as shown oversimplified in Figure 1), and there are 20 minutes' worth of electrodeposition to be scraped off when the point (or rather the leading edge of the point) 4a returns to that element. The carrier 4 preferably flies back to its starting point or may move upwards and downwards (20 minutes each) at the same speed. Even while scraping is proceeding, the current is maintained at substantially 5.7A; a smooth cathode could pass only 0.8A at that voltage.

Turning to Figure 2, a cathode is shown identical to that in Figure 1, but the scraper differs. The scraper 14 is in the form of a helical blade making just one rotation in the height of the cathode and driven by a slow-speed motor 15 at one revolution per 20 minutes.

Any other powder removal method which substantially maintains the roughness of the electrodeposit would be expected to be suitable, such as blasting by gas or liquid or solid; vibration (e.g. ultrasonics).

A part-height or helical scraper fractures off the dendritic electrolytic deposits, leaving a beneficial underlying micro-roughness; a full-length scraper might bare the cathode and even burnish it, whereby the current density would regress to that described in relation to a brand new cathode. This fracturing action also has the advantage of yielding a powder product reasonably consistent in size and type.

If the frequency with which the scraper traverses any given point on the cathode is too low, and trials will readily establish this, the electrodeposit becomes excessively rough and the energy required to rotate the rough cathode becomes correspondingly excessive. For some metals and electrolytes, this excessive roughness takes the form of spindly dendrites which can drop off randomly and which are of inconsistent quality. They can drop off in such a way as to lead to a 'peeling' of the electrodeposit; in catastrophic cases, up to 10% of the burden can be shed in this way, unbalancing the cathode to the detriment of its driving mechanism. The spindly dendrites may also damage any nearby diaphragm or membrane.

CLAIMS

1. An electrodeposition cell having a rotating cylindrical deposition electrode and a means for removing deposit from that electrode, the means being characterised in that, in operation, the electrode retains a substantially rough electrodeposit.

2. A cell according to Claim 1, characterised in that the means is a scraper (4) engaging the electrodeposit and breaking away its outer portion.

3. A cell according to Claim 2, characterised in that the axial extent of the engaging part (4a, 14) of the scraper does not exceed half the axial extent of the electrode (1), the engaging part being axially movable so that, with the electrode rotating, the scraper can engage any point on the electrodeposit.

4. A cell according to Claim 3, characterised in that the axial extent of the engaging part (4a, 14) of the scraper does not exceed 0.1, preferably 0.01, of the axial extent of the electrode (1).

5. A cell according to Claim 4, wherein the axial extent of the engaging part (4a, 14) of the scraper does not exceed 0.002 of the axial extent of the electrode (1).

6. A cell according to any of Claims 2 to 5, wherein the scraper (4) is axially movable.

7. A cell according to any of Claims 2 to 5, wherein the scraper comprises a rotatable helical blade (14) whose axis is parallel to the cylinder axis.

8. A method of removing deposit from a rotating cylindrical deposition electrode in an electrodeposition cell during electrodeposition, characterised in that the electrode retains a substantially rough electrodeposit.

9. A method according to Claim 8, wherein the method of removal comprises air-blasting or vibration.

10. A method according to Claim 8, wherein the method of removal comprises applying to the electrodeposit, such that it will not bare the electrode, a scraper breaking away the outer portion of the electrodeposit.

11. A method according to Claim 10, wherein the scraper scrapes not more than 0.1 of the cylindrical area of the electrode in one revolution thereof.

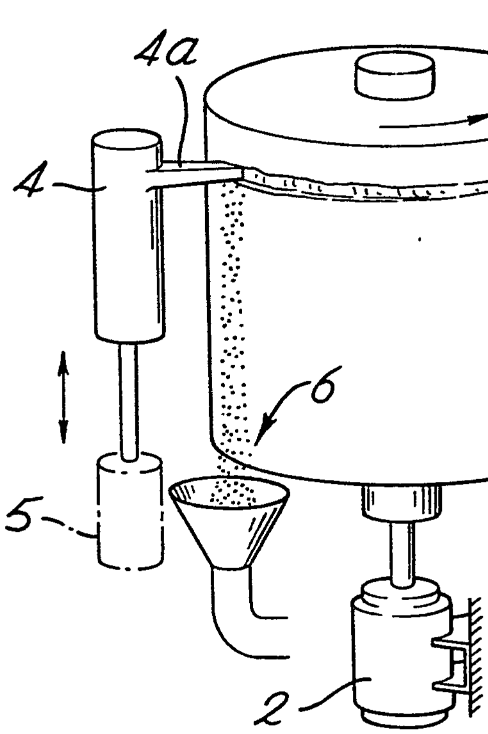

Fig. 1

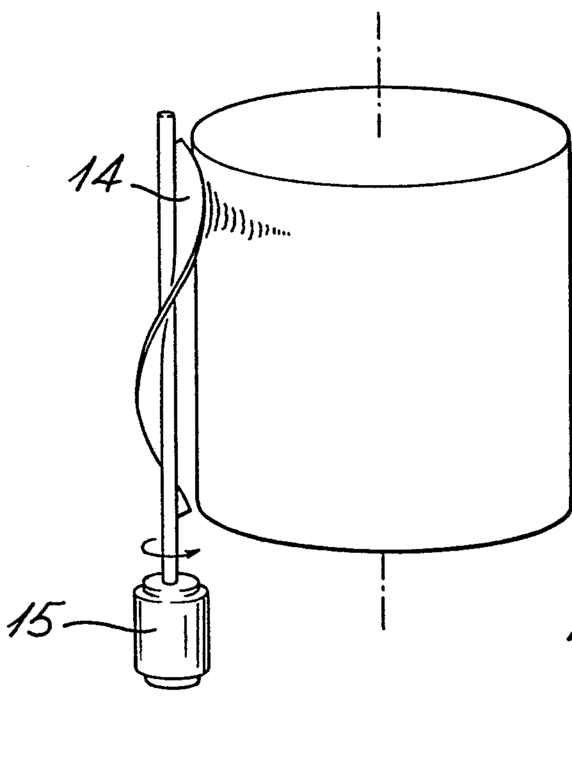

Fig. 2

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European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 82 30 0710

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Y	DE-A-2 048 600 (EISNER) *Page 8, lines 17 to 29; page 9, lines 1 to 4; pages 19 and 20; claims*	1	C 25 C 7/00 C 25 C 5/02
Y,D	FR-A-2 302 353 (NATIONAL RESEARCH DEVELOPMENT CORPORATION) *Page 13, lines 13 to 34; figures 1 and 2* & GB - A - 1 505 736	1	
X	US-A-1 535 577 (A.H.WYLD CLEAVE) *Page 2, lines 95 to 130; figures 1 and 5,6*	1,2,8, 10	
Y	FR-A-2 449 734 (DUDUCO) *Page 5, lines 9 to 14*	1,8	
A	FR-A-1 264 597 (J.PRUNET)		

TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

C 25 C 7
C 25 C 5

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27-05-1982	GROSEILLER PH.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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