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Applicant : **NORANDA INC.**
BCE Place,
181 Bay Street,
Suite 4100
Toronto Ontario, M5J 2T3 (CA)

Inventor : **Houlachi, George**
12 Maple
Sainte Anne de Bellevue, Quebec H9X 2E4
(CA)
Inventor : **Agnew, Michael J.**
46 Bourbonnais C.P. 296
Côteau du Lac, Quebec J0P 1B0 (CA)

Representative : **Des Termes, Monique**
c/o Société de Protection des Inventions
25, rue de Ponthieu
F-75008 Paris (FR)

Production of compact zinc deposits from alkaline electrolyte.

A process for the production of compact zinc deposits from alkaline electrolyte comprises electrowinning zinc from an alkaline electrolyte contained in an electrolysis cell while strongly agitating the electrolyte adjacent the cathode of the cell. The electrolyte consists of 10 to 80 g/L zinc and an equivalent hydroxide ion level to dissolve the zinc. The temperature of the electrolyte is maintained in the range of 25 to 60°C and the current density above 500 A/m². The electrolyte is agitated at an angular velocity of 500 to 10,000 rpm which may be translated to a linear velocity of 0.5 to 10 m/s adjacent the cathode.

This invention relates to the production of compact zinc deposits from alkaline electrolyte.

Background of the Invention

5 During zinc electrolysis from alkaline electrolyte, zinc is deposited onto the cathode in the form of powder. Powdery zinc deposits, typical of electrolysis from alkaline medium, are easily oxidized resulting in a difficult to melt zinc product necessitating costly multistage post processing steps.

The alkaline zinc leach/electrolysis process has recently been selected as the most promising process to recover zinc from galvanized steel scrap. The low solubility of iron in alkaline medium allows for recovery of zinc without attacking the iron substrate. Recovery of zinc is effected by electrolysis after purifying the electrolyte by cementation onto zinc powder. The technical viability of the process was proven in pilot plant scale, and this process is now considered by the steel producers as the most promising technology for dezincing galvanized steel scrap. Due to the reasons mentioned above, recovery of zinc in powder form affects the marketability of the zinc product and in turn the economics of the process.

15 Several scenarios have been proposed for marketing the zinc powder such as in application for paints. However, this market is limited and still requires a strict control of the physical and chemical properties of the recovered zinc powder. The possibility of melting the zinc powder in presence of various fluxes has also been considered with limited success and extra cost to the process. Controlling the oxidation of zinc powder during electrolysis and processing of the product could also be practised with limited success. There is, therefore, a need to identify a method of producing compact zinc deposits which would provide with a full credit for the recovered zinc thus facilitating the recycling of zinc in an economical viable manner.

20 Other needs for such technology include the zinc refining whereby a low voltage, high intensity and high faradaic yields will be desirable. Recovery of zinc from alkaline zinc batteries in a solid compact form will also facilitate the recycling of zinc in this application.

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Statement of the Invention

The process in accordance with the present invention comprises electrowinning zinc from an alkaline electrolyte contained in an electrolysis cell while strongly agitating the electrolyte adjacent the cathode of the cell. The electrolyte consists of 10 to 80 g/L zinc and an equivalent hydroxide ion amount to dissolve the zinc. The electrolyte is maintained at a temperature between 25 and 60°C and the current density at about 500 A/m² up to 3000 A/m² depending on the rate of agitation of the electrolyte.

30 The preferred temperature of the electrolyte is about 25°C and the current density about 1500 A/m².

The zinc level in the electrolyte is preferably between 40 and 60 g/L.

35 The electrolyte agitation is in the range of 500 to 10,000 rpm which may be translated to a linear velocity of 0.5 to 10 m/s. The angular velocity is preferably above 1000 rpm, specifically when operating at high current densities.

The above conditions were found to result in recovering zinc in compact form similar to that obtained from acid sulphate electrolyte.

40 The above process can be carried out in an electrolytic cell allowing for continuous plating of zinc in strip form and peeling off the deposited zinc. The recovered zinc product, in strip form, can then be easily melted and reutilized in industry without the problems experienced with the oxidized zinc powder.

Brief description of the drawings

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

Figure 1 is a schematic diagram of an experimental cell used to carry out the process in accordance with the present invention;

50 Figure 2 is a schematic diagram of an electrolysis cell for carrying out continuous plating and stripping of compact zinc from alkaline electrolyte; and

Figures 3 and 4 show Scanning Electron Microscope photographs depicting respectively, the microstructure of zinc deposits in the form of zinc powder and in the compact crystalline form.

55 Detailed Description of the Invention

Laboratory scale electrolysis tests in alkaline medium showed that the morphology of zinc deposits could be changed to compact zinc deposits by increasing the agitation of the electrolyte adjacent to the cathode

substrate. The experiments were carried out in an electrolytic cell 10 as shown in Figure 1 using a rotating cylinder electrode 12 mounted on the shaft 14 of a rotor 16 rotating at 2000 rpm. Current from a power supply 18 was applied between a cylindrical anode 19 and the cathode 12 over a 2 to 3 hours of electrolysis using a synthetic alkaline electrolyte. The electrolyte contained 40 to 60 g/L of zinc and 200 to 300 g/L of NaOH. The solution temperature was varied from 25 to 50°C and the current density from 500 to 2000 A/m². At the end of the test the deposit was removed from the cathode, weighed for current efficiency determinations and its morphology was assessed.

Experimental Results

Effect of electrolyte agitation (cathode rotation)

Electrolysis tests carried out under static conditions with no agitation of the electrolyte resulted in powdery zinc deposits such as shown in Figure 3. The tests were conducted at an applied current density of 500 A/m² for one hour of deposition at a solution temperature of 25 and 40°C. Increasing the agitation to 500 rpm improved the deposit morphology while areas of powder zinc still appeared at the surface of the cathode. Operating above 1000 rpm the deposit morphology was smooth and free of powdery spots such as shown in Figure 4. These results clearly demonstrate the beneficial effect of electrolyte agitation on the morphology of zinc deposits.

Effect of deposition time

The effect of deposition time was investigated under the experimental conditions given above. The results of these tests showed that the deposit morphology remained intact producing compact zinc deposits over a 3 hour of deposition time at a current density of 1000 A/m², and 2 hours at 1500 A/m². At this electrolysis duration, the thickness of the deposits was about 1.5 to 2 mm which is adequate for continuous deposition and stripping of the recovered zinc. Longer deposition times are possible for small depletion levels of zinc in solution. When operating at low zinc levels in solution the morphology of the zinc deposits deteriorates resulting in formation of zinc powder. It is, therefore, important as in all zinc electrowinning processes to operate at an optimum zinc to caustic ratio in order to obtain compact zinc deposits.

Effect of solution temperature

The effect of two solution temperatures (25 and 40°C) on the morphology of zinc deposits was investigated. The results showed that at 40°C, the morphology of the zinc deposits was slightly affected resulting in signs of corrosion. This effect was not observed at 25°C. When operating at high solution temperatures, it is possible, by modifying the electrolysis conditions, as for example the duration of the deposition time, to produce compact zinc deposits. As operation at lower solution temperatures does not cause any problem in the overall process efficiency, it is recommended that for optimum results regarding the morphology of the zinc deposits to electrowin at lower solution temperatures.

Effect of current density

The effect of current density on the morphology of the zinc deposits was evaluated. It was shown that operating at a current density of 500 to 3000 A/m² results in production of compact zinc deposits. Under the conditions studied during this investigation, it was found that at high current density of 3000 A/m² some dendrite formation at the edges of the cathode was observed. Operation at high current densities did not improve the morphology of the zinc deposits obtained at 40°C. It is possible, however, to operate at high current densities with corresponding strong solution agitation. Most of the work carried out in this investigation was conducted at 1500 A/m² which represents a three fold increase in current density as compared to the conventional zinc electrowinning process in acidic zinc sulphate electrolyte. Optimum current density is determined by the requirements of the specific process, capital cost and energy consumption during electrolysis.

Effect of zinc depletion

Experiments were carried out to determine the effect of zinc and hydroxide ion level in the solution on the morphology of zinc deposits. The initial zinc concentration was 60 g/L and NaOH 300 g/L. The test was conducted under the following operating conditions:

current density: 1500 A/m²
 agitation of the cathode: 2000 rpm
 temperature: 25°C

5 The results of these tests as shown in Table I indicate that the zinc deposit remained compact while depleting zinc to 20 g/L from an initial value of 60 g/L. At this zinc concentration, the level of NaOH was 349 g/L.

TABLE I

Zn g/L	NaOH g/L	Cell Voltage	Current Efficiency %	Morphology
60-55	300-306	3.06	100	Compact
55-50	306-312	3.07	100	Compact
50-45	312-318	3.7	100	Compact
45-40	318-324	3.10	100	Compact
40-35	324-330	3.10	100	Compact
35-30	330-337	3.10	99.8	Compact
30-25	337-342.8	3.15	99.8	Compact
25-20	342.8-349	3.15	99.8	Compact

25 The above results showed that the present method of electrowinning zinc from alkaline medium, while producing compact zinc deposits, can be used over a wide range of zinc ion concentration thus facilitating the operation of preceding unit operation steps such as the leaching step in the dezincing of galvanized steel scrap process.

Effect of cycles of zinc deposition/dissolution

30 Electrolysis tests were carried out using the same electrolyte after correcting for the zinc level in solution by dissolving an equivalent amount of ZnO. The tests were conducted by electrowinning zinc to 40 g/L over a period of four hours followed by dissolving ZnO to correct the zinc and hydroxide concentration to its initial level of 60 and 300 g/L respectively.

35 The test conditions were the same as those described in the previous paragraph. The results of these tests as shown in Table II indicate that during four complete cycles of electrolysis/leach, the deposit morphology was not affected resulting in formation of compact zinc deposits. These tests simulated the sequence of steps normally used in industry such as the electrolytic production of zinc by hydrometallurgical methods. Similar conditions are also observed in the alkaline dezincing process for treating galvanized steel scrap.

40 Table II

Cycles	Zn g/L	NaOH g/L	Cell Voltage V	Current Efficiency %	Morphology
1	60-40	300-324	3.10	100	Compact
2	60-40	300-324	3.10	100	Compact
3	60-40	300-324	3.10	100	Compact
4	60-40	300-324	3.10	100	Compact

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Optimum Process conditions

55 Based on the above results, it was shown that zinc can be electrowon from alkaline medium in compact form using strong electrolyte agitation. The best results obtained show that the morphology of the zinc deposits is smoother and more compact when operating at a low electrolyte temperature of 25°C and at a current density of 1500 A/m². Regarding the zinc level in solution, it was shown that operating between 60 and 40 g/L results in smooth and compact zinc deposits. Lower zinc levels (20 g/L) were also used with good results.

The conditions mentioned above provide the range of optimum operating conditions. However, good results were also obtained at conditions within the following ranges:

Electrolytic temperature:	25 to 60°C
Current density:	500 to 3000 a/m ² depending on rate of cell agitation
5 Zinc level:	10 to 80 g/L
Hydroxide ion level:	equivalent to dissolve the zinc
Electrolyte agitation:	angular velocity of 500 to 10,000 rpm or linear velocity of 0.5 to 10 m/s

The above process was demonstrated under laboratory batch conditions. The results can be translated to continuous operating conditions using an electrolysis cell design rendering possible the continuous plating and stripping of the zinc deposit.

The angular velocity in rpm for the rotating cylindrical cathode can be expressed in terms of linear velocity (m/s) using the value of the periphery of the cylinder and the number of revolutions per minute. These values can then be used in a more classical electrolysis cell design whereby high electrolyte flow rates can be achieved.

The laboratory system of electrolysis comprised a rotating cylinder having dimensions of 1.74 cm in diameter and 2.5 cm in height. The total surface area of the cathode was 13.659 cm². Electrode rotation at 1000 rpm can then be translated to 0.91 meter/second. This relative cathode velocity can be applied to a modified electrolysis cell used in the electrogalvanizing industry. A schematic of the electrolytic cell is shown in Figure 2. The cell comprises a slow moving cathode 20 which could be made of a stainless steel belt attached to two rotating drums 22. Two stationary anodes 24 are placed along side of the moving cathode. The electrolyte is pumped in a launder 26 at the top of the cell and is flown by gravity between the cathode and the anode. The linear velocity of the electrolyte passing through a narrow interelectrode spacing can reach values up to 10 m/s thus promoting favourable mass transfer condition. Zinc is plated onto the moving cathode and is continuously stripped using a specially designed doctor blade 28 located at the upper rotating drum. This design and other similar electrolysis cells system used in the electrogalvanizing industry can be used for the production and recovery of compact zinc deposits from alkaline medium.

Claims

1. A process for the production of compact zinc deposits from alkaline electrolyte, comprising electrowinning zinc from an alkaline electrolyte contained in an electrolysis cell provided with a cathode and an anode and consisting of 10 to 80 g/L zinc and an equivalent hydroxide ion level to dissolve the zinc, the temperature of the electrolyte being in the range of 25 to 60°C and the current density above 500 A/m², while agitating the electrolyte at an angular velocity of 500 to 10,000 rpm which may be translated to a linear velocity of 0.5 to 10 m/s adjacent the cathode.
2. A process as defined in claim 1, wherein the electrolyte temperature is about 25°C.
3. A process as defined in claim 1 or 2, wherein the current density is about 1500 A/m².
4. A process as defined in claim 1, wherein the zinc level is between 40 and 60 g/L.
5. A process as defined in claim 1, wherein the electrolyte agitation is between 1000 and 3000 rpm depending on the applied current density.
6. A process as defined in claim 1, wherein the electrolyte cell is a cell allowing for continuous plating of zinc in strip form and peeling off the deposited zinc.

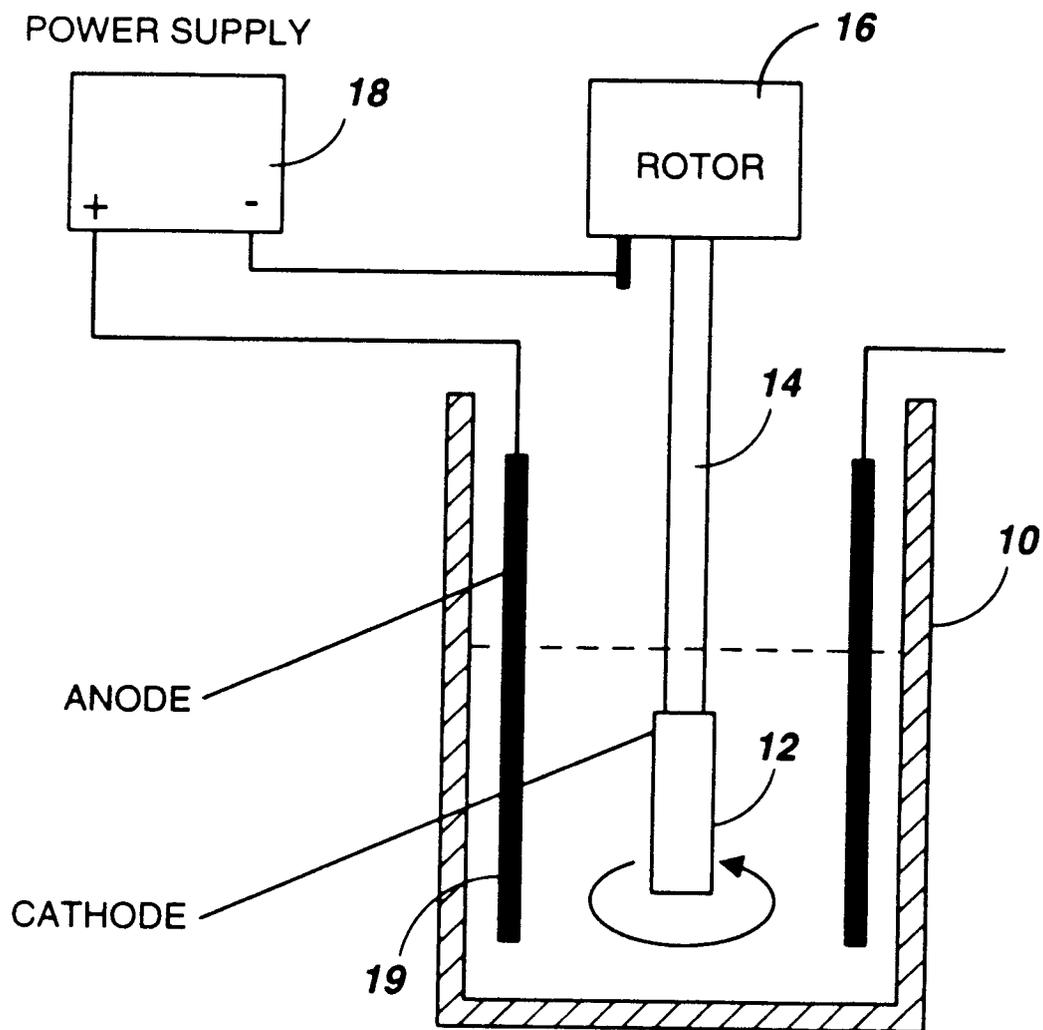


Fig. 1

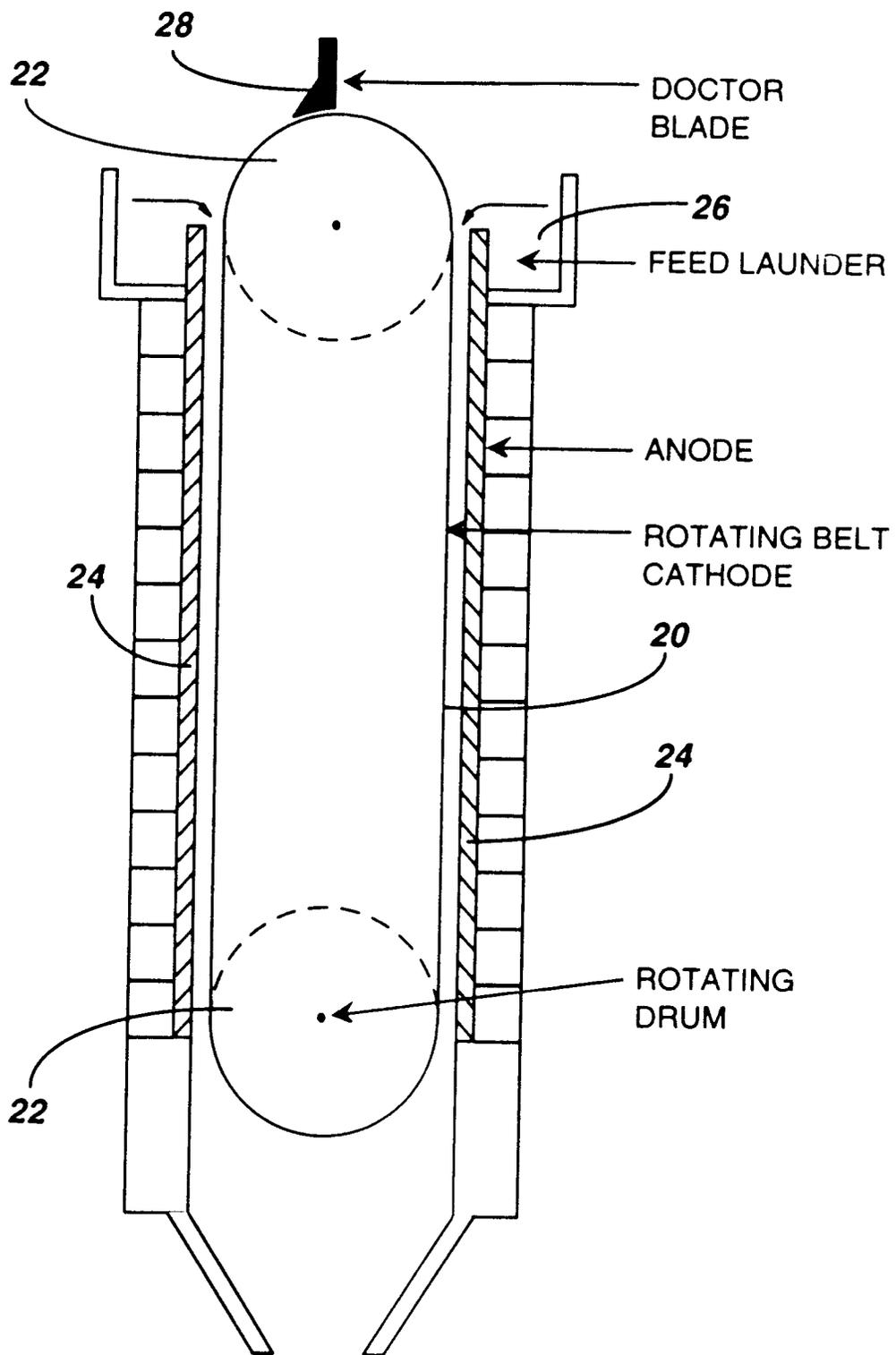


Fig. 2

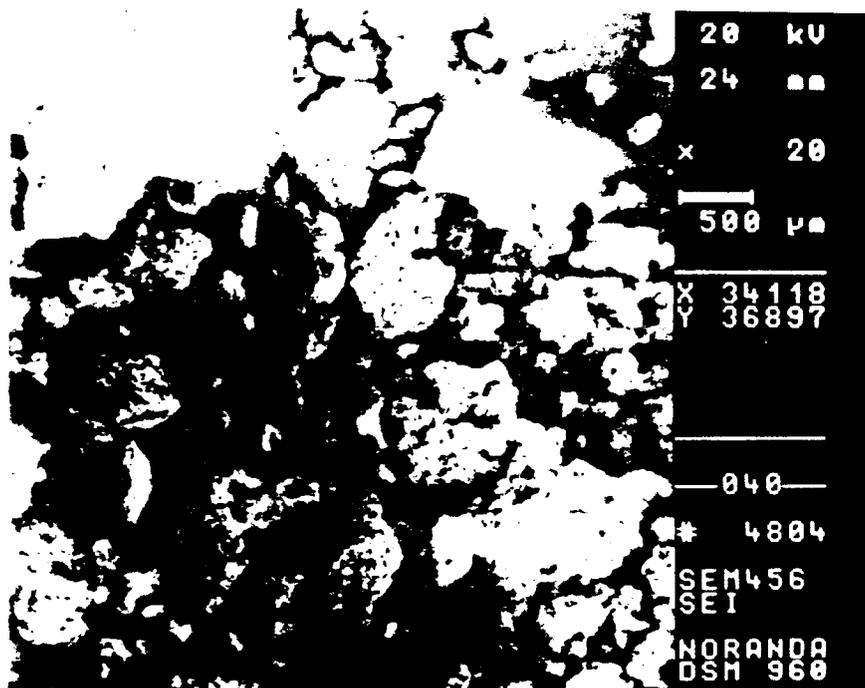


Fig. 3

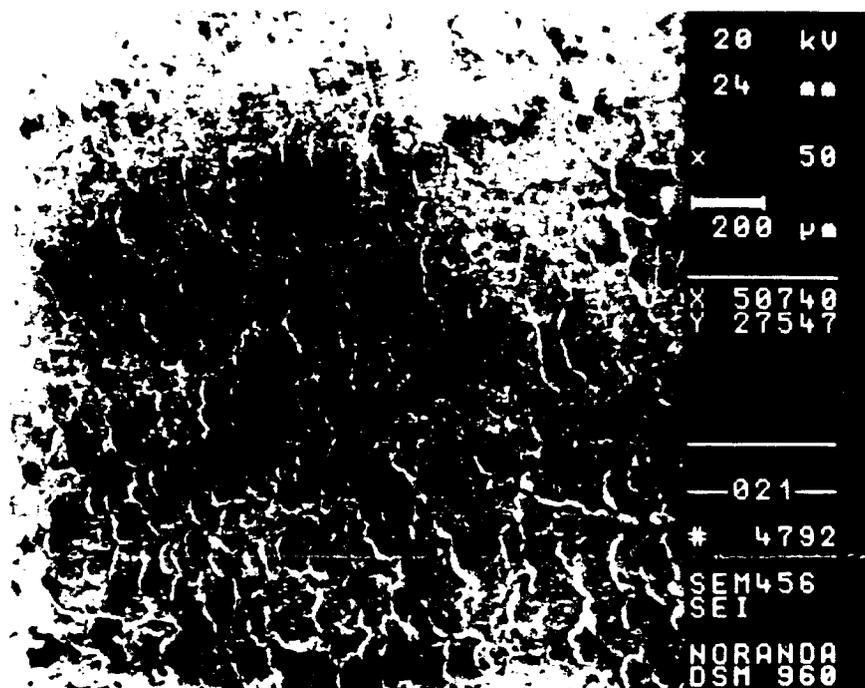


Fig. 4



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 40 2732

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.5)
X	DE-A-27 39 970 (S.E.P.R.E.Z.) 16 March 1978 * page 20, line 14 - line 22 * * page 23, line 20 - line 24 * * page 29, line 26 - page 30, line 6 * * figures 3,5 * -----	1,3,4,6	C25C1/16
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C25C
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	15 February 1994	Groseiller, P	
CATEGORY OF CITED DOCUMENTS		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	
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