(11) **EP 2 987 893 A2**

(12)

EUROPEAN PATENT APPLICATION published in accordance with Art. 153(4) EPC

(43) Date of publication: 24.02.2016 Bulletin 2016/08

(21) Application number: 14785891.4

(22) Date of filing: 09.04.2014

(51) Int Cl.: **C25C** 7/06 (2006.01)

(86) International application number: PCT/CL2014/000013

(87) International publication number:
WO 2014/169400 (23.10.2014 Gazette 2014/43)

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Designated Extension States:

BA ME

(30) Priority: 16.04.2013 CL 2013001048

(71) Applicant: New Tech Copper S.p.A. Santiago (CL)

(72) Inventors:

 AYLWIN GÓMEZ, Pedro Alejandro Macul, Santiago (CL)

- LAGOS LAGOS, Nicolás Ignacio Macul, Santiago (CL)
- LÓPEZ PARRAGUEZ, David Fernando Santa Cruz, VI región (CL)
- CORTÉS BUSCH, Sergio Eduardo Macul, Santiago (CL)
- ESCOBAR CÉLÈRY, Hernán Alejandro Santa Cruz, VI región (CL)
- (74) Representative: Delorme, Nicolas et al Cabinet Germain & Maureau BP 6153 69466 Lyon Cedex 06 (FR)

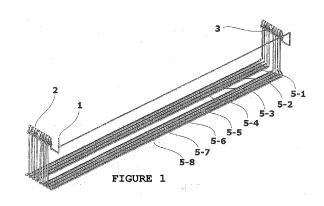
(54) SYSTEM OF AIR-SPARGING VALVES IN ELECTROLYTIC CELLS, WHICH REDUCE PRODUCTION LOSSES CAUSED BY BREAKS OR PHYSICAL DAMAGE, AND OPERATING METHOD

(57) The punched pipes or microporous hoses used to bubble air located on the floor of the electrolytic cells for metals production are exposed to breakage or physical damages by the accidental fall of anodes, cathodes on them or by the premature release of part of the cathode deposition as well as by damages produced by intervention inside the cells.

Said damages force to at least stop the air bubbling, damaging the quality of the metal produced to stop the production process for its repair with the consequent loss of production.

The valves system of this invention located at the entrance of the front and rear air distributors as well as in both ends of each of the punched pipes or microporous hoses, allows the insulation of each of these pipes or hoses from the system and do continue the air bubbling even in the case of damage or breakage of one or more of them, making the production without air bubbling less frequent as well as the downtime of the operation to repair the damages, thereby decreasing the production losses.

The operation procedure starts with the identification of the air injection line that failed, followed by the closing of the front and rear valves of said line, then with the visual inspection to check that the size and uniformity of the bubble is restored.



35

40

45

DESCRIPTION OF WHAT IS KNOWN IN THE ART

1

[0001] The electrolytic deposit of metals from solution is normally done in masonry cells coated with electricity insulating materials, acid or alkali-resistant or temperature resistant.

[0002] In these cells the fresh electrolyte is fed through one longitudinal end of the Cell while the worn electrolyte is discarded by the bottom opposite longitudinal end if the feeding was done through the upper part or viceversa.

[0003] Occasionally the transverse circulation of the electrolyte has been used, i.e. parallel to the faces of the anodes and cathodes with piping with holes located in front of each space inter-anode-cathode, that are placed longitudinally through the bottom at one side of the cell. Through this piping the fresh electrolyte is introduced, while the discharge is done by overflow, or through the other punched piping located at the opposite upper side of the cell.

[0004] In order to improve the electricity efficiency, to avoid the deposition of metal on the vertical borders of the cathodes, to improve the quality of the cathode deposit and to decrease the production losses due to the cells maintenance, now removable insulating structures are being used with electrode guides to put position anodes and cathodes as disclosed in the Chilean Patent 45288 (application 1020-2004).

[0005] With the same previous objectives, air or other gases are often injected to shake the electrolyte and to make its concentration more uniform which helps to prevent the crystallization of the electrolyte and to decrease the effect of the limit layer. This can be done introducing punched tubes at the bottom of the cell through which air or other gases is injected, which requires the use of fans, feeding ducts and the distribution punched pipes.

[0006] The fact of having pipes with gases sunken in the electrolyte make them tend to float making the fixation systems of the pipes to the cell complex.

In recent years, the bubbling of air is done using microporous hoses as a standard of the process since they have the advantage over the punched pipes of allowing a better control of the bubbling characteristics. These microporous hoses like the punched pipes are installed longitudinally on the floor of the cell or next to it, they are normally fed through both ends in order to share the loss of pressure that occurs in the pipes or hoses as the air flows towards the center of the cell.

[0007] During normal operation, the failure in the air distribution through the air distributors to their microporous hoses, arises from their physical fatigue, either because of material failure, bumps, accidental fall of anodes or cathodes on the pipes, because of the accidental fall of part of a cathode deposit; the breakage due to the stretching by a hook used to remove solids from inside the cell, that by doing it blindly the operation can cause

that when rising the hook it tugs some of the microporous hoses (5) shown in Figure 1/7, stretching that also damages the front and the rear distribution heads as shown in Figures 2a/7, 2b/7, 3a/7 and 3b/7.

[0008] In order to extend the shell life of the microporous hoses as well as of the punched pipes, attempts have been made to physically protect them with coatings of different types without having effectively solved the issues to date.

[0009] In order to control the gas flow sprayed to a distribution system and provide exit openings in the distributing system in order that the fresh electrolyte currents and spraying gas from said exit opens go in a relatively uniform way through the cathodes of the cell, a method as the one described in the Chilean Patent application 200202154 was developed.

[0010] Another method to operate a cell that incorporates bubbling gas is described in the Chilean Patent Application 200402120. In the National Search no insulation or protection methods against damages of pipes or microporous hoses of the distribution systems of bubbling gas in electrolytic cells were found.

[0011] In the International Search, the physical protection for pipes and hoses refer preferably to cover completely those elements with an upper coating like the one disclosed in the Chinese Patent Application CN201593667(U), a lower curved protection to protect the radius of curvature in a horizontal plane, leaving the horizontal diametric plane upwards uncovered as in the Chinese Patent Application CN202040482U, a complete protection of the flexible element (electric conductor or hose) with a corrugated metal coating or a flexible mesh similar to the ones used in the flexible unions used in plumbing to prevent a radial expansion like the one described in the German Patent Application DE102008049497 (A1). Another protection method consists of wrapping with a tape made of elastic material and shock absorbent arranged in a spiral on the surface of the hose as disclosed in the German Patent Application DE 10 2009 053092 A1. Another form of hose protection consists of covering with one or more concentric metal springs arranged in spiral over the hose like the ones used in some connections in automotive hydraulic breaks pipes as disclosed in the Chinese Patent Application CN201925657U. Another way to protect curved hoses is disclosed in the Japanese Patent Application JP2008223940 that covers with one or two moulded circular layers that can be easily separated in fractions.

DESCRIPTION OF THE DRAWINGS

[0012]

Figure 1/7 shows an isometric view of the air supply network, in a quasi isobaric version.

Figure 2a / 7 shows an isometric view of the front end of the air supply network.

55

15

20

25

35

40

45

50

55

3

cover above the air distributor.

Figure 3a / 7 shows an isometric view of the rear end of the air supply network.

Figure 3b / 7 shows an isometric view of the rear end of the air supply network, including a protective cover of the rear air distributor.

Figure 4/7 shows a cross section view of an electrolytic cell incorporating inside, a removable insulating structure for anodes and cathodes positioning.

Figure 5/7 shows a partial isometric view of the front end of the removable insulating structure for anodes and cathodes positioning, in which the vertical guides for cathodes can be observed.

Figure 6/7 shows a perspective view of the removable insulating structure for anodes and cathodes positioning, in which the vertical guides for cathodes are not shown.

Figure 7/7 shows a flowchart for the operation of the valve system to keep the bubbling of air or gas running in metal electrolytic production cells

[0013] The numbers shown in the figures have the following meaning:

- (1) Air inlet.
- (2) Front air distributor.
- (3) Rear air distributor.
- (4) Air distributor protective cover.
- (5-1) Microporous hose in first position.
- (5-2) Microporous hose, in second position.
- (5-3) Microporous hose, in third position
- (5-4) Microporous hose, in fourth position.
- (5-5) Microporous hose, in fifth position.
- (5-6) Microporous hose, in sixth position.
- (5-7) Microporous hose, in seventh position.
- (5-8) microporous hose, in eighth position.
- (6) Electrolyte feeding pipe to the cell.

- (7) Cathode.
- (8) Cathode support bar.
- (9) Cathode guide.
 - (10) Masonry cell.
 - (11) Plenum collector by acid mist suction.
 - (12) Electrolyte level.
 - (13) Cathode lower guide.
- (14) Microporous hose support.
 - (15) Support borehole for the microporous hose path.
 - (16) Lower longitudinal frame, of the removable insulating structure for anodes and cathodes positioning.
 - (17) Lateral diagonal frame, of the removable insulating structure for anodes and cathodes positioning.
 - (18) Front horizontal frame, of the removable insulating structure for anodes and cathodes positioning.
 - (19) Upper longitudinal frame, of the removable insulating structure for anodes and cathodes positioning.
 - (20) Rear vertical frame, for the removable insulating structure for anodes and cathodes positioning.
 - (21) Anode lower guide.
 - (22a)Air stopcock to the air front manifold.
 - (22a-1) Stopcock of the air front manifold to the pipe and microporpous hose in first position.
 - (22a-2) Stopcock of the air front manifold to the pipe and microporpous hose in second position.
 - (22a-3) Stopcock of the air front manifold to the pipe and microporpous hose in third position.
 - (22a-4) Stopcock of the air front manifold to the pipe and microporpous hose in fourth position.
 - (22a-5) Stopcock of the air front manifold to the pipe and microporpous hose in fifth position.
 - (22a-6) Stopcock of the air front manifold to the pipe and microporpous hose in sixth position.

3

20

(22a-7) Stopcock of the air front manifold to the pipe and microporpous hose in seventh position.

(22a-8) Stopcock of the air front manifold to the pipe and microporpous hose in eighth position.

(22p) Air stopcock to the air rear manifold.

(22p-1) Stopcock of the air rear manifold to the pipe and microporpous hose in first position.

(22p-2) Stopcock of the air rear manifold to the pipe and microporpous hose in second position.

(22p-3) Stopcock of the air rear manifold to the pipe and microporpous hose in third position

(22p-4) Stopcock of the air rear manifold to the pipe and microporpous hose in fourth position

(22p-5) Stopcock of the air rear manifold to the pipe and microporpous hose in fifth position

(22p-6) Stopcock of the air rear manifold to the pipe and microporpous hose in sixth position

(22p-7) Stopcock of the air rear manifold to the pipe and microporpous hose in seventh position

(22p-8) Stopcock of the air rear manifold to the pipe and microporpous hose in eighth position

(23) Anode.

(24) Bubbling electrolysis system in operation

(25) Failure of the air injection line.

(26) Regular bubbling continued.

(27) Identification of the line that failed.

(28) Closing of Front and Rear valves of the line that failed

(29) Visual inspection to check if the size and uniformity of the bubbles were restored.

(30) Hoses damaged less than 40%.

(31) Stop of the electrolysis and repair of the damaged hoses.

DESCRIPTION OF THE INVENTION

[0014] This invention consists of a system of multiple air stopcocks (22a, 22a-1, 22a-2, 22a-3.. to 22a-n, and 22p, 22p-1, 22p-2, 22p-3... to 22p-n, wherein "n" equals

the number of bubblers used such as microporous punched pipes or microporous hoses, forming ordered pairs of valves), located at the entrance of each distributor (2), (3) and at the front and rear entrance of each punched pipe or microporous hose (5-1, 5-2, 5-3,... to 5-n), used to bubble air or gas to a metal production electrolytic cell, in order to put out of service one or the two distributors, or one or more air bubbling hoses that are damaged or destroyed, thereby it is possible to continue to operate the cell with a minimum decrease in the quality of the cathode deposition.

[0015] The technical issue solved by this invention consists of avoiding or decreasing the loss of quality/production produced when stopping the operation to repair damages or breakages of the air or gas bubbling distribution hoses; the damages produced by cathodes falls; the partial detachment of the cathode deposit on them; or the manipulation of several tools used to remove solids from the bottom of the cell, as well as to guarantee the operation of the air bubbling system in the same conditions as it was designed, independently of the damage that might be exerted on its aeration networks.

[0016] Another approach attempted to solve this same technical issue has consisted of physically protecting the external part of the punched pipes or microporous hoses; anyhow none of the systems used so far to protect the punched pipes or microporous hoses from damages, as described in what is known in the art, has proved to be satisfactory for this application, where the protection should allow the controlled release of bubbling gas in the cell while in operation.

[0017] One of the major advantages of this system is that by leaving out of operation the failing or broken porous hose, by closing the valves located at the front and rear air inlet, it is possible to delay the cell operation downtime by two, three and even four times the average failure time of a traditional cell without the valves system of this invention, with a minimum decrease in the quality of the cathode deposition.

[0018] The operating procedure for the readjustment of the air or inert gas injection lines, starts with the normal operation of the plant. The air or inert gas is injected through bubbling elements (air or inert gas injection lines), such as microporous hoses or punched pipes, at the start-up. Later, due to various reasons such as cathodes fall, the partial detachment of the cathode deposition on the bubbling lines, or because of the poor handling of various tools used to remove solids from the bottom of the cell, the bubbling lines suffer irreparable damages. Therefore, in order to maintain the quality of the generated cathode deposition, it is necessary to adjust the aeration or gas injection lines, in order to keep a constant and uniform bubbling flow. In order to do this, the identification of the line where the failure occurred is done and consequently the one through which the air or inert gas leaks. The procedure consists of individually closing the pair of valves of each line and leave the other lines with their valves opened, and make a visual inspection to de-

20

25

termine whether the bubbling returns to its normal characteristics regarding the uniformity and size of the bubble. Once the line is identified it is kept with its pair of valves closed and the normal cell electrowinning operation continues. This procedure is repeated each time a line failure is detected or when the bubbling does not exhibit the same characteristics it had at the beginning of the operation.

[0019] Some traditional ways to carry out this invention are described below.

[0020] One embodiment of this invention, without thereby losing its generality, is shown in Figure 1/7, which includes eight microporous hoses (5-1) to (5-8), a front air distributor (2), a rear air distributor (3), and air stopcocks to the front (22a) and rear(22p) entrances of the distributors and stopcocks to the front entrance (22a-1) up to (22a-8) and to the rear entrance (22p-1) up to (22p-8) of each of the hoses (5-1) to (5-8). When a significant air loss occurs in one of the hoses, its identification is done and then the front and rear stopcocks of the damaged branch are closed, which is done without the need of stopping the operation of the cell.

[0021] Another embodiment of this invention, is shown in Figures 2b/7 and 3b/7 in which a protective cover is included (4) to protect the valves from bumps or accidental fall of heavy elements or objects used in the electrolytic plants.

APPLICATION EXAMPLE

[0022] In order to prove the usefulness of this invention a pilot quasi-isobaric feeding net was built such as the one shown in Figure 1/7, consisting of a straight grid with 8 microporous hoses.

[0023] The quasi-isobaric grid is mounted on the structure shown in figure 6/7 which corresponds to a removable insulating structure to position anodes and cathodes. In this structure each hose is inserted in one of the boreholes (15) as can be seen in Figure 4/7. Once beaded the eight microporous hoses of the quasi-isobaric feeding net in the boreholes of the supports (14), they are connected to 8 ducts of rigid plastic material located at the front end and at the rear end of the removable insulating structure to position anodes and cathodes that go up to its upper part as can be seen in Figure 5/7. Each of the rigid plastic material ducts are connected through a ball valve (22a) and (22p) to the air distributors (2) and (3) shown in Figure 1/7, located at the front and rear end of the device, subsequently connecting the isobaric feeding to the air general feeding (1) indicated in Figures 1/7, 2a/7 and 2b/7.

[0024] Once all the quasi-isobaric air feeding net is mounted on the removable insulating structure to position anodes and cathodes indicated in Figure 6/7 and also partially shown in Figure 5/7, all the set is installed inside the masonry electrolytic cell (10).

[0025] Once the above is done, the air entrance to the fan of the plant that supplies the bubbling gas was con-

nected, then 61 insoluble anodes and 60 stainless steel cathodes, spaced at 100 mm between cathodes centers, this number is fixed by the distance between the cathodes guides positions (9) of the removable insulating structure to position anodes and cathodes.

[0026] Then the cell was filled with electrolyte and was connected to the electric power to deposit metal on the cathodes thereby starting the feeding of electrolyte and bubbling gas.

[0027] The operating conditions were set at 2 volts between anodes and cathodes and electrolyte circulation at 30m/hour and bubbling gas feeding at 15 cum per hour. Then the microporous hoses was damaged (5-2) breaking it, followed by the closing of the stopcocks (22a-2) and (22p-2) in each end of the broken hose. The flow was kept at 15 cum per hour and the operation pressure of the system changed from 1,090 hectopascals to 1,100 hectopascals of absolute pressure and the bubbling process maintained its quality in terms of bubble size, number of them observed and uniformity of the bubbling. There was no loss of gas through the broken hose after the closing of the corresponding valve which permitted to continue with the operation until it finished despite the failure.

[0028] The procedure was repeated breaking a second hose, (5-7) and closing the valves (22a-7) and (22p-7), and the feeding of bubbling gas flow was kept the same. This time the operating pressure was changed from the 1,100 hectopascals to 1,110 hectopascals of absolute pressure. Again, the bubbling process maintained its quality in terms of the size of the bubble, the number of bubbles observed and the uniformity of the bubbling. No gas loss was observed through any of the damaged hoses.

[0029] After the damages intentionally produced as described above, the operation ran with no interruption until the process was finished and the crop was done in the regular way without inconveniences with regards to the quality of the cathodes obtained.

[0030] After multiple experiences performed, suggestion is to stop the operation to repair the air distribution system when more than 40% of the hoses are damaged, thereby anticipating the moment when the quality of the bubbling decreases and starts to affect the process.

Claims

45

50

55

1. Punched hoses or microporous hoses system used for air or gas bubbling to the electrolyte of a metals production cell installed at the bottom or near the bottom of a cell or of a removable insulating structure to position anodes and cathodes, located inside the cell for the continuous operation regardless of the damage that may be exerted on the aeration nets CHARACTERIZED in that it has multiple air stopcocks located at the entrance of the bubbling gas feeding distributors as well as at both ends of each one of the punched pipes, punched hoses or microporous hoses.

- 2. Punched hoses or microporous hoses system used rous hoses.
 - for air or gas bubbling to the electrolyte of a metals production cell installed at the bottom or near the bottom of a cell or of a removable insulating structure to position anodes and cathodes, located inside the cell for the continuous operation regardless of the damage that may be exerted on the aeration nets of Claim 1, CHARACTERIZED in that it has protection on the air feeding distributors located at both ends of the punched piping, punched hoses or micropo-
- 3. System operation method of Claim 1 CHARACTER-**IZED** in that it comprises the following steps:
 - -bubbling through the air or inert gas feeding net; - failure or breakage of an air or inert gas injection line of the air or inert gas feeding net, produced by the fall of cathodes, partial detachment of the cathode deposit on them or the deficient manipulation of several tools used to remove solids from the bottom of the cell:
 - identification of the line with the air or inert gas leak by individually closing a pair of component valves of the line and subsequent visual inspection of the bubbling;
 - closing of the valves connected to the line with the failure;
 - if cumulatively the damaged elements of the air or inert gas feeding net is equal or higher than 40 per cent, the electrolysis is stopped and the repair of the damaged elements is done; if it is less than 40 per cent, the aeration or gas injection process is continued normally.

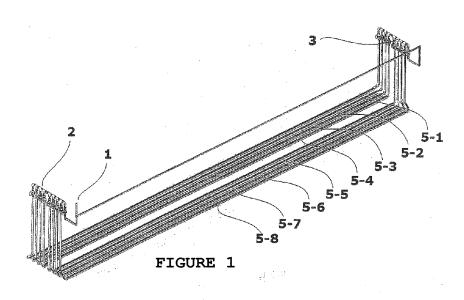
15

40

45

50

55



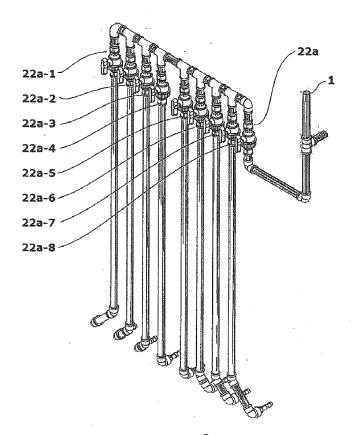
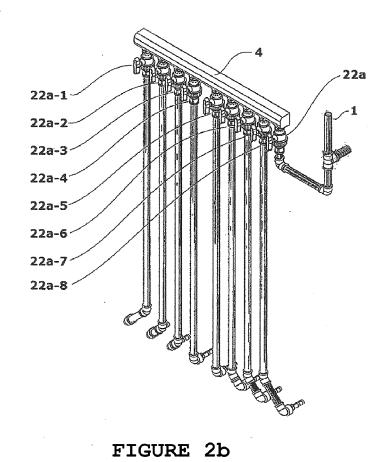


FIGURE 2a



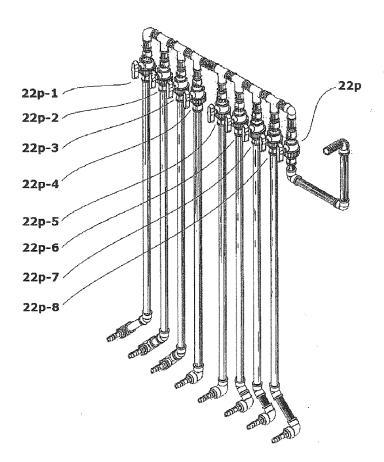


FIGURE 3a

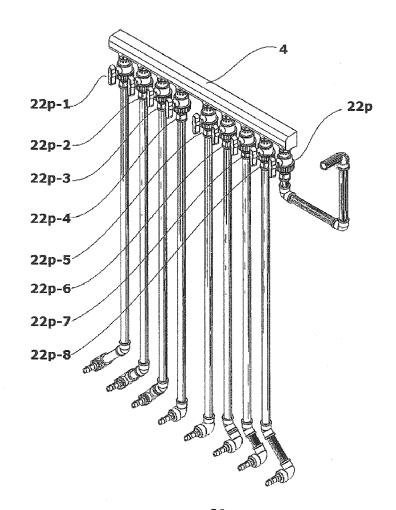


FIGURE 3b

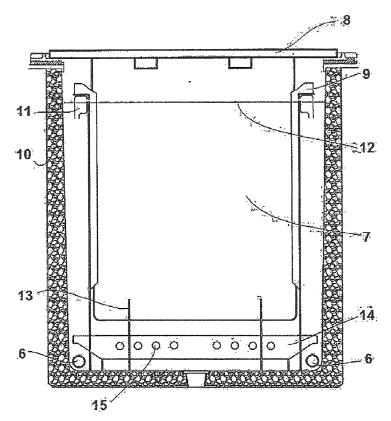


FIGURE 4

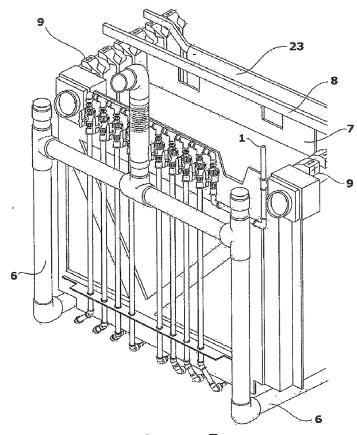
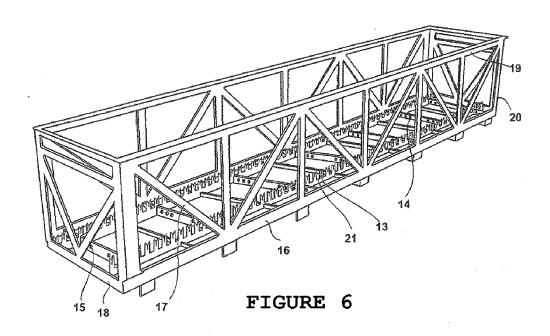
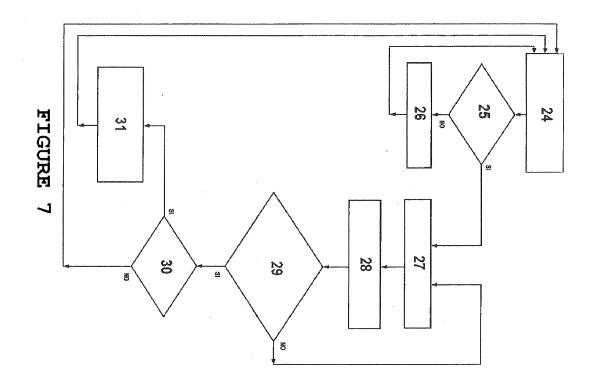


FIGURE 5





EP 2 987 893 A2

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- CL 45288 [0004]
- CL 10202004 [0004]
- CL 200202154 [0009]
- CL 200402120 [0010]
- CN 201593667 U [0011]

- CN 202040482 U [0011]
- DE 102008049497 A1 [0011]
- DE 102009053092 A1 [0011]
- CN 201925657 U [0011]
- JP 2008223940 B **[0011]**