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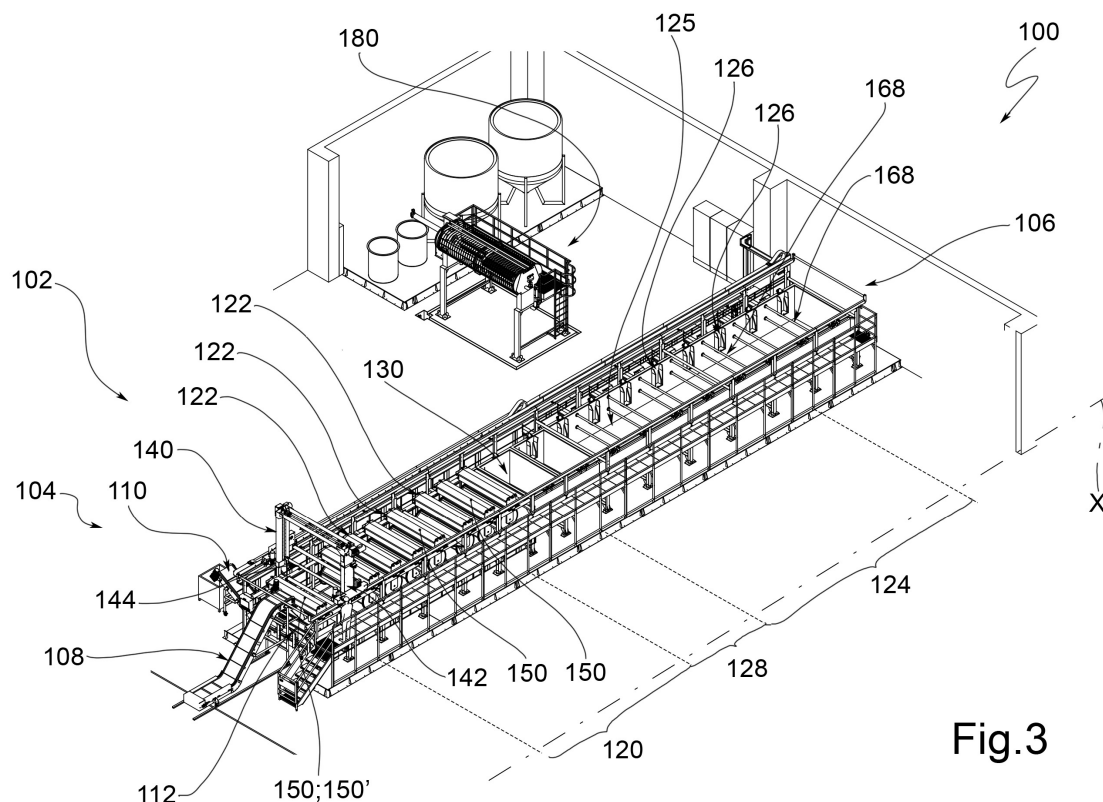
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(54) **ELECTROCHEMICAL PROCESS AND PLANT FOR DETINNING SRAPS OF COPPER OR ALLOYS THEREOF**

(57) The present invention relates to an industrial plant (100) for electrochemically detinning tinned, or tinned and sheared, scraps of copper or alloys thereof, using an electrolyte solution (16) of potassium chloride

(KCl) and/or ammonium chloride (NH₄CL) and/or sodium chloride (NaCl) and/or calcium chloride (CaCl₂), and the relative electrochemical detinning process.

**Fig.3**

Description

Technical field

[0001] The present invention belongs to the field of processes and plants for recovering non-ferrous scraps; in particular, the object of the present invention is an electrochemical process and a plant for detinning tinned, sheared scraps of copper and alloys thereof.

Background art

[0002] The term "sheared tinned scraps of copper and alloys thereof" is commonly used to indicate fragments of electronic components, such as electrical connectors, terminals, circuitry and the like, consisting of a substrate of copper or copper alloys, for example brass, coated with a layer of tin, usually required to enhance the corrosion resistance of the component. Tin is applied to the copper substrate by means of some processes such as electrochemical tinning and tin brazing. Generally, such fragments have a size of a few centimeters per side, generally from 5 to 1000 millimeters.

[0003] The recycling of such scraps is of particular importance for recovering both the substrate and the tin. However, the presence of tin requires specific processing to separate the two metals and obtain materials of high quality for reuse. To this end, it is necessary to subject the scraps to a detinning process for removing tin from the surface of the substrate.

[0004] One of the needs of the sector is to have a detinning process capable of obtaining a practically pure material of the substrate, since tin is generally an undesirable contaminant in recycled copper, negatively influencing properties thereof such as electrical conductivity and corrosion resistance.

[0005] Several detinning processes are known today.

[0006] The most widespread processes for industrial exploitation are of the electrochemical type and provide for the tin-coated copper fragments to be immersed in a solution of strong acids. However, such processes use highly polluting acids, such as sulfuric or hydrochloric acid, and therefore have an unsustainable environmental impact, as well as high costs for disposal of spent solutions and management of fumes.

[0007] Detinning processes of the chemical type are also known, in which solutions of strong acids or strong bases are used, capable of dissolving tin from the surface of the copper substrate. Such processes, however, are particularly slow and unsuitable for an economically profitable industrial exploitation, in addition to presenting high costs for the disposal of spent solutions and for the management of fumes.

[0008] Detinning processes of the mechanical type, in which the fragments are ground, and of the thermal type, in which the fragments are subjected to pyrolysis, are also known; both such types, however, are not sui-

table to obtain high-quality recycled copper, since unacceptable quantities of tin remain associated with the copper substrate.

[0009] Therefore, the need is felt to have an industrial plant and a process for detinning sheared tinned scraps of copper and alloys thereof which are industrially exploitable and have a low environmental impact.

Object of the invention

[0010] It is the object of the present invention to achieve an electrochemical detinning process and a corresponding plant which meet the needs of the sector, with particular reference to industrial exploitation, and which overcome the drawbacks mentioned with reference to the prior art.

[0011] Such object is achieved by an industrial plant according to claim 1 and by the corresponding electrochemical detinning process. The dependent claims identify further advantageous features of the invention.

Brief description of the drawings

[0012] The features and advantages of the process and of the plant according to the present invention will be apparent from the following description, given by way of nonlimiting example and not by way of limitation, in accordance with the Figures of the accompanying drawings, in which:

- Figure 1 diagrammatically shows a fragment of a sheared tinned scrap of copper;
- Figure 2 diagrammatically shows an electrolytic cell for the electrochemical process according to the present invention;
- Figure 3 diagrammatically shows a plant according to the present invention;
- Figures 4a and 4b show a roto-elevator device of the plant;

Detailed description

[0013] By way of example, Figure 1 shows a fragment 1 of a sheared tinned scrap of copper, consisting of a substrate 2 of copper or copper alloy, for example brass, superficially coated with a layer 4 of tin. The layer 4 of tin adheres to the surface of the substrate 2 of copper or copper alloy.

[0014] In accordance with Figure 2, an electrolytic cell 10 for a detinning process according to the present invention comprises a positively charged anode connected to a plurality of fragments 1 by means of an anode electrode 12, a negatively charged cathode connected to a cathode body 14, for example consisting of a steel or stainless steel body, and an electrolyte solution 16 in which the fragments 1 and the cathode body 14 are immersed.

[0015] According to an aspect of the invention, the

electrolyte solution 16 is a solution containing one or more chlorides selected from the group comprising potassium chloride (KCl), ammonium chloride (NH_4Cl), sodium chloride (NaCl) and calcium chloride (CaCl_2). An electrolyte solution of potassium chloride (KCl) and/or of ammonium chloride (NH_4Cl) has proved particularly suitable for the objects of the present invention.

[0016] Such solutions are practically neutral (pH7 as the potassium chloride solution) or weakly acidic (pH between 5 and 7, as the ammonium chloride solution).

[0017] Preferably, the electrolyte solution 16 has a concentration of at least 1M (1 Molar = 1 mole of solute/liter of solvent).

[0018] Advantageously, the Applicant has found that an electrochemical detinning process with an electrolyte solution of KCl and/or NH_4Cl is particularly advantageous in treating sheared tinned scraps of copper, since it makes it possible to separate practically all the tin from the substrate surface, rapidly and using electrolyte solutions which are reusable or else easily disposable and of low environmental impact.

[0019] At the end of the treating cycle, a sludgy precipitate 18 deposits in the electrolyte solution 16, containing tin, in addition to any further elements, such as, for example, potassium (K) and chlorine (Cl) originating from the electrolyte solution, and, for example, zinc (Zn) and/or copper (Cu) in the event that the substrate 2 of the fragments 1 have also been attacked.

[0020] The process according to the present invention therefore makes it possible to obtain detinned copper or copper alloy fragments and a precipitate from which, when suitably refined, it is possible to extract the tin.

[0021] Preferably, furthermore, the detinning process provides agitation of the electrolyte solution, for example of the mechanical type, by means of an agitator 13, or of the fluid-dynamic type, by means of nozzles capable of injecting further electrolyte solution into the electrolyte solution.

[0022] Advantageously, the Applicant has observed an improvement in the effectiveness of the process, with the other conditions being equal, due to the agitation of the electrolyte solution during the detinning.

[0023] Preferably, furthermore, the electrolytic cell 10 comprises a basket 20 for containing the electrolyte solution 16. The basket 20 is configured so that the surfaces in contact with the electrolyte solution are of polymer material resistant to the oxidizing action of the electrolyte solution.

[0024] For example, said polymer material is selected from the group comprising polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE; Teflon), epoxy resins, elastomers.

[0025] Advantageously, the use of a basket made of polymer material makes it possible to considerably extend the service life of the basket, since it is unaffected by the oxidation of the electrolyte solution.

[0026] According to an alternative embodiment, the electrolytic cell 10 comprises heating means, for example electric resistors 22, suitable for heating the electrolyte solution up to a predefined temperature.

[0027] Advantageously, the Applicant has found that as the temperature of the electrolyte solution increases, for example between 30° and 60°, the detinning process is more effective.

[0028] Preferably, furthermore, the electrolytic cell comprises mechanical removal means configured to operate on the tin layer adhered to the substrate to separate it therefrom. For example, said mechanical removal means comprise a sound wave emitter for removing the tin adhering to the substrate by means of sonication, or a rotating container, generally referred to as a tumbler or roto-tumbler or barrel or roto-barrel, inside which the fragments 1 are contained. Inside the roto-barrel, the fragments hit one another and against the walls of the roto-barrel itself, thus undergoing friction leading to the mechanical removal of the tin still adhered to the substrate.

[0029] Advantageously, the Applicant has observed that the use of mechanical removal from electrochemically treated scraps is particularly effective, since the action of the electrolyte solution is particularly effective in the initial steps of the process, whereas subsequently, to remove the oxidized tin, still adhered to the substrate, the mechanical removal intervention is appropriate.

[0030] Preferably, furthermore, the electrolytic cell 10 comprises an adjustment device 22 comprising acidity adjustment means 24 suitable for introducing into the electrolyte solution contained in the basket 20 an additive, for example hydrochloric acid (HCl), capable of increasing the acidity of the solution to restore an optimal pH value.

[0031] The Applicant has in fact found that, as the detinning processes follow one another, the electrolyte solution, reusable per se, undergoes a slight basification. It is therefore appropriate to restore the optimal value of the pH by adding an acid additive.

[0032] According to an alternative embodiment, the adjustment device 22 comprises acidity detection means 26 suitable for automatically detecting the pH of the electrolyte solution, operatively connected to the adjustment means 24 to introduce the appropriate quantity of additive.

[0033] Preferably, furthermore, the electrolytic cell 10 comprises a sacrificial anode 28 consisting of copper or zinc, connected to the anode electrode 12 and to the fragments 1. This makes it possible to limit the electrochemical action on the copper of the substrate of the fragments.

[0034] In accordance with Figure 3, by way of example, an industrial electrochemical plant 100 for detinning sheared tinned copper fragments 1 comprises a main line 102 extending along a longitudinal line axis X between an inlet and outlet section 104 for loading the

sheared tinned scraps and unloading the detinned fragments, and an opposite end section 106.

[0035] Preferably, the inlet and outlet section 104 comprises an inlet belt 108, preferably as an ascending ramp, an outlet belt 110, preferably as an ascending ramp, and a loading and unloading station 112, feedable by the inlet belt for loading the tinned scraps and served by the outlet belt for removing the detinned fragments.

[0036] The main line 102 further comprises a storage section 120 arranged downstream of the inlet and outlet section 104; the storage section 120 comprises a plurality of storage seats 122, arranged in sequence along the line axis X.

[0037] Furthermore, the main line 102 comprises a treatment section 124 downstream of the inlet and outlet section 104 and preferably downstream of the storage section 120. The treatment section 124 comprises a treatment tank 125 in which the electrolyte solution is contained and a plurality of treatment seats 126, arranged in the treatment tank 125, in sequence along the line axis X, up to the end section 106.

[0038] The treatment section 124 further comprises at least one cathode electrode 168, usually consisting of a steel cable coated with polymer material up to the treating tank 125, and a crosspiece or steel plate which forms the cathode body inside the treatment tank 125, connected to the cable and arranged so as to be immersed in the electrolyte solution.

[0039] Preferably, furthermore, the main line 102 comprises a washing section 128 downstream of the inlet and outlet section 104, preferably downstream of the storage section 120, and upstream of the treatment section 124. The washing section 128 comprises at least one washing tank 130, arranged along the line axis X between the loading and unloading station 112 and the treatment tank 125.

[0040] The plant 100 further comprises at least one movement device 140. The movement device 140 comprises a gantry structure 142 operable in horizontal translation along the line axis X between the inlet and outlet section 104 and the end section 106, and a picker 144 placed on board the gantry structure 142 and operable in vertical translation.

[0041] The plant 100 further comprises at least one roto-barrel or roto-tumbler 150 for containing and re-mixing the tinned scraps. Preferably, the plant 100 comprises a plurality of roto-barrels 150.

[0042] Each roto-barrel 150 (Figures 4a and 4b), comprises a crosspiece 152 such that, when the roto-barrel 150 is engaged with the main line 102, extends along a transverse direction and is suitable for mechanically engaging with and disengage from the picker 144 of the movement device 140.

[0043] The roto-barrel 150 further comprises a rotating container 154, operatively supported by the crosspiece 152 to rotate in a controlled manner along a barrel axis Z, parallel to the transverse direction.

[0044] The roto-barrel 150 further comprises at least one electric motor 156 onboard the crosspiece 152 and a transmission mechanism 158, preferably gear-based, for transmitting rotary motion from the electric motor 156 to the rotating container 154.

[0045] According to a preferred embodiment, the rotating container 154 comprises an annular side wall 160, preferably coaxial with the barrel axis Z, provided with a plurality of holes or slots, configured for the passage of the electrolyte solution and the retention of tinned scraps or detinned fragments. Preferably, the side wall 160 has a polygonal cross-section, for example hexagonal, heptagonal or octagonal.

[0046] Preferably, furthermore, the rotating container 154 comprises a left base 162 and a right base 164 which close the container at the transverse ends. Preferably, at least one of said left base 162 and right base 164, preferably both, consists of a gear of the transmission mechanism 158, coaxial with the barrel axis Z.

[0047] The rotating container 154 further comprises, on the side wall 160, an access group 166 openable for loading the tinned scraps into the rotating container 154 and reclosable so as to prevent an accidental escape thereof.

[0048] Preferably, the rotating container 154 is entirely made of polymer material. For example, the polymer material is selected from the group comprising polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE; Teflon), epoxy resins, elastomers.

[0049] Furthermore, the roto-barrel 150 comprises an anode electrode 170, usually consisting of a steel cable coated with polymer material, entering the rotating container 154, immersed in the scraps loaded into the container; preferably, at the end of the anode electrode a sacrificial anode of copper or zinc is placed.

[0050] According to a preferred embodiment, the roto-barrel 150 comprises a plurality of nozzle groups 172 suitable for injecting further electrolyte solution into the electrolyte bath, to obtain an agitation of the electrolyte solution.

[0051] According to a further embodiment, the plant 100 comprises a filter press 180 to which the precipitate that has accumulated in the tank is supplied; the filter press presses and filters the precipitate, so as to remove the electrolyte solution and obtain blocks intended for subsequent refining for the extraction of tin.

[0052] According to further alternative embodiments, the plant comprises said heating means and/or said adjustment device.

[0053] During normal operation of the plant 100, in a first configuration or loading configuration, an empty roto-barrel 150' is accommodated in the loading and unloading station 112 in an arrangement such that the access group 166 of said empty roto-barrel 150' is facing upwards so as to allow loading.

[0054] The rotating container 154 of said empty roto-barrel 150' is loaded with sheared, tinned scraps of

copper and alloys thereof, preferably by means of the inlet belt 108. Therefore a roto-barrel full of tinned scraps is obtained.

[0055] The movement device 140 is configured to pick up the roto-barrel full of tinned scraps, lifting it up by virtue of the engagement of the picker 144 to the crosspiece 152 of the roto-barrel, and to move it towards the treatment section 124 by virtue of the translation of the gantry structure 142.

[0056] Once at a predetermined treatment seat 126 of the treatment tank 125, the movement device 140 deposits the full roto-barrel in said treatment seat 126; the rotating container 154 of the roto-barrel is thereby at least partially immersed in the electrolyte solution.

[0057] Once the electrolyte solution and the operating parameters are set, such as current and voltage (for example, a current between 1 and 2000A and a voltage from 1 to 50V, according to the plant), acidity and possibly the temperature of the solution, the electrolytic detinning treatment is initiated by means of the application of a desired potential difference between the cathode electrode and the anode electrode of the full roto-barrel.

[0058] According to a first alternative embodiment of the detinning process, while the rotating container 154 is immersed in the electrolyte solution and the potential difference is applied, the rotating container 154 is driven in rotation, continuously over time or for predefined time intervals, possibly reversing the rotation direction, thus causing the mixing and the mutual rubbing of the tinned scraps.

[0059] According to a further alternative embodiment of the detinning process, the rotating container is periodically withdrawn from the electrolyte solution and while it is outside thereof, it is driven in rotation, to then be immersed again.

[0060] After a predefined time interval, the detinning treatment having ended, the precipitate is accumulated in the treatment tank 125 and the roto-barrel is full of detinned copper fragments.

[0061] The movement device 140, which in the meantime has possibly moved other roto-barrels, picks up the roto-barrel filled with detinned fragments, and moves it towards the inlet and outlet section 104.

[0062] Preferably, in the path from the treatment seat 126 to the inlet and outlet section, the movement device 140 makes a stop in the washing section 128 to immerse and raise the roto-barrel in a predefined washing tank 130 to wash the detinned fragments from the electrolyte solution.

[0063] Finally, the movement device 140 places the roto-barrel full of detinned fragments, preferably washed, in the loading and unloading station 112.

[0064] With the access group 166 of the roto-barrel unlocked, a rotation of the rotary container 154 brings said access group 166 to the lower part, causing the discharge of the detinned fragments onto the outlet belt 110, which provides for the removal.

[0065] According to production scheduling, the movement device may carry a roto-barrel full of tinned scraps to the storage section, for example in the case where all the treatment seats are occupied, and pick up a roto-barrel full of tinned scraps from the storage section to bring it to the treatment section when a treatment seat becomes free.

[0066] Or, according to the production scheduling, the movement device may take a roto-barrel filled with detinned fragments, possibly washed, to the storage section, for example in the case where the loading and unloading section is occupied, and pick up a roto-barrel filled with detinned fragments from the storage section to bring it to the loading and unloading section when it becomes available.

[0067] Innovatively, the electrochemical detinning process and the electrochemical plant according to the present invention meet the needs of the sector, since they make it possible to obtain fragments of high-quality copper or alloys thereof, substantially uncontaminated by tin, by means of a process with low environmental impact.

[0068] Advantageously, furthermore, the invention makes it possible to recover the tin separated from the scraps and precipitated.

[0069] The present invention also applies to the electrochemical detinning of tinned scraps of copper or alloys thereof, even if not sheared.

[0070] It is apparent that, in order to meet contingent needs, those skilled in the art may make changes to the above-described process and plant, all contained within the scope of protection as defined by the following claims.

Claims

1. An industrial plant (100) for electrochemically detinning tinned, or tinned and sheared, scraps of copper or alloys thereof, comprising a treatment tank (125) containing an electrolyte solution (16) of potassium chloride (KCl) and/or ammonium chloride (NH₄Cl) and/or sodium chloride (NaCl) and/or calcium chloride (CaCl₂), and at least one roto-barrel (150) comprising a perforated rotating container (154), configured to be immersed into the electrolyte solution and operable in rotation for mixing the scraps, wherein the roto-barrel (150) comprises an anode electrode (170), consisting of a conductive cable entering the rotating container (154), configured to be immersed into the scraps loaded in the container, and wherein a sacrificial anode made of copper or zinc, configured to be immersed into the scraps, is connected to the end of the anode electrode.
2. A plant according to claim 1, wherein the rotating container is made of polymer material, preferably

selected from the group comprising polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE; Teflon), epoxy resins, elastomers.

3. A plant according to claim 1 or 2, wherein the rotating container (154) comprises an annular side wall (160) provided with a plurality of holes or slots for the passage of the electrolyte solution. 5
4. A plant according to claim 3, wherein the side wall (160) has a polygonal cross-section, for example hexagonal, heptagonal, or octagonal. 10
5. A plant according to any one of the preceding claims, comprising a cathode electrode (168) provided with one or more conductive bodies placed in the treatment tank (125). 15
6. A plant according to any one of the preceding claims, wherein the roto-barrel (150) comprises at least one nozzle group (172) configured to inject additional electrolyte solution into the electrolyte solution. 20
7. A plant according to any one of the preceding claims, comprising a filter press for the precipitate. 25
8. A plant according to any one of the preceding claims, comprising filtering and recirculation means for filtering and reintroducing the electrolyte solution into the treatment tank. 30
9. A plant according to any one of the preceding claims, comprising a device for adjusting the acidity of the solution. 35
10. A plant according to any one of the preceding claims, comprising: 40
 - a main line (102) extending along a longitudinal line axis (X) between an inlet and outlet section (104) for loading sheared tinned scraps and unloading detinned fragments, and an opposite end section (106); 45
 - a storage section (120) arranged downstream of the inlet and outlet section (104) for storing roto-barrels (150);
 - a treatment section (124) downstream of the inlet and outlet section (104) and of the storage section (120), comprising the treatment tank (125); 50
 - a washing section (128) downstream of the inlet and outlet section (104) and of the storage section (120) and upstream of the treatment section (124); 55
 - at least one movement device (140) for moving the roto-barrels (150).

11. A process for electrochemically detinning tinned, or tinned and sheared, scraps of copper or alloys thereof, carried out by means of the industrial plant according to any one of the preceding claims.

12. A roto-barrel (150) comprising a perforated rotating container (154), configured to contain and retain, during a rotation, tinned, or tinned and sheared, scraps of copper or alloys thereof, and to be immersed into an electrolyte solution (16) of potassium chloride (KCl) and/or ammonium chloride (NH₄Cl) and/or sodium chloride (NaCl) and/or calcium chloride (CaCl₂), wherein the rotating container is made of polymer material, preferably selected from the group comprising polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE; Teflon), epoxy resins, elastomers.

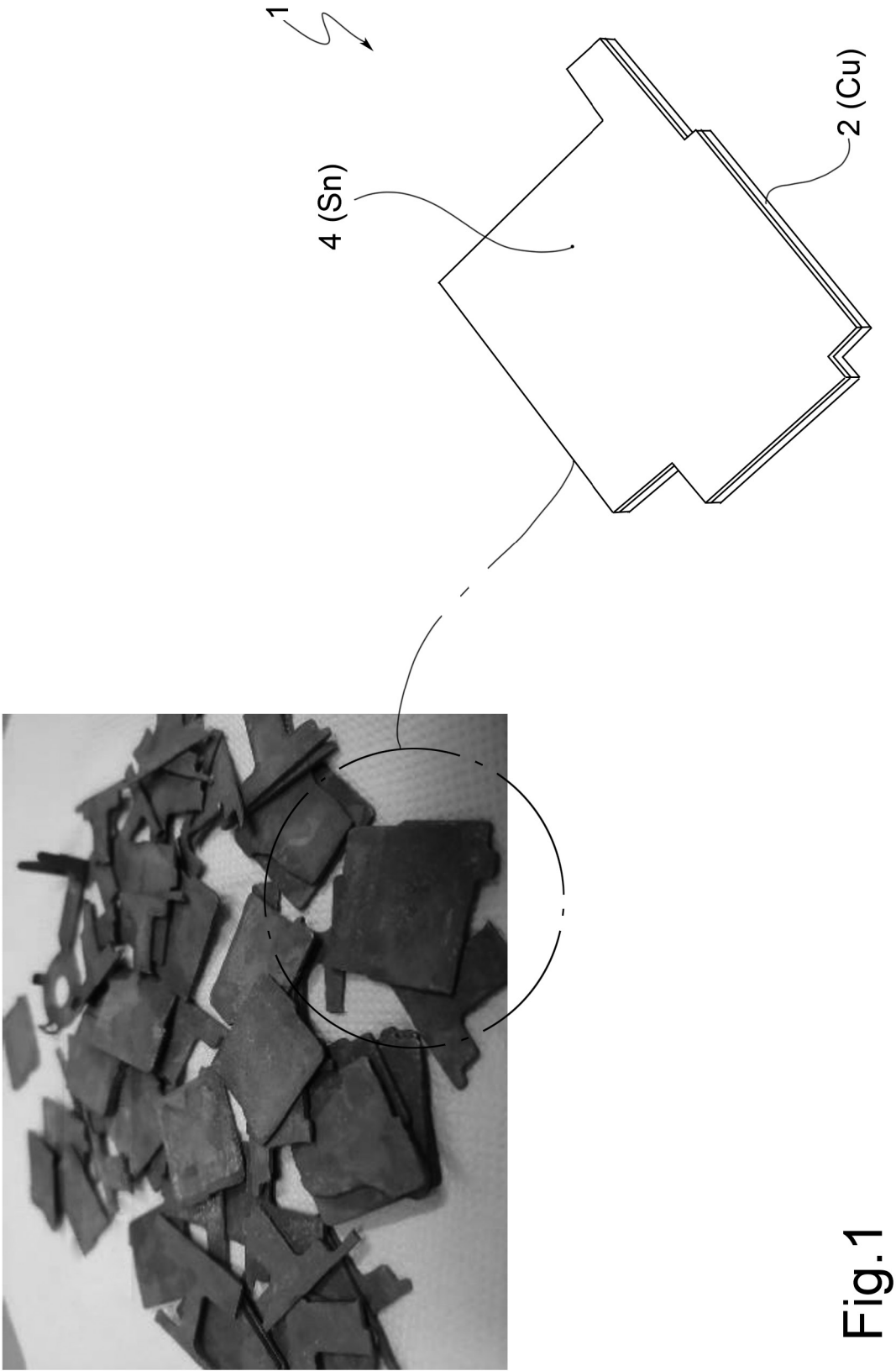


Fig.1

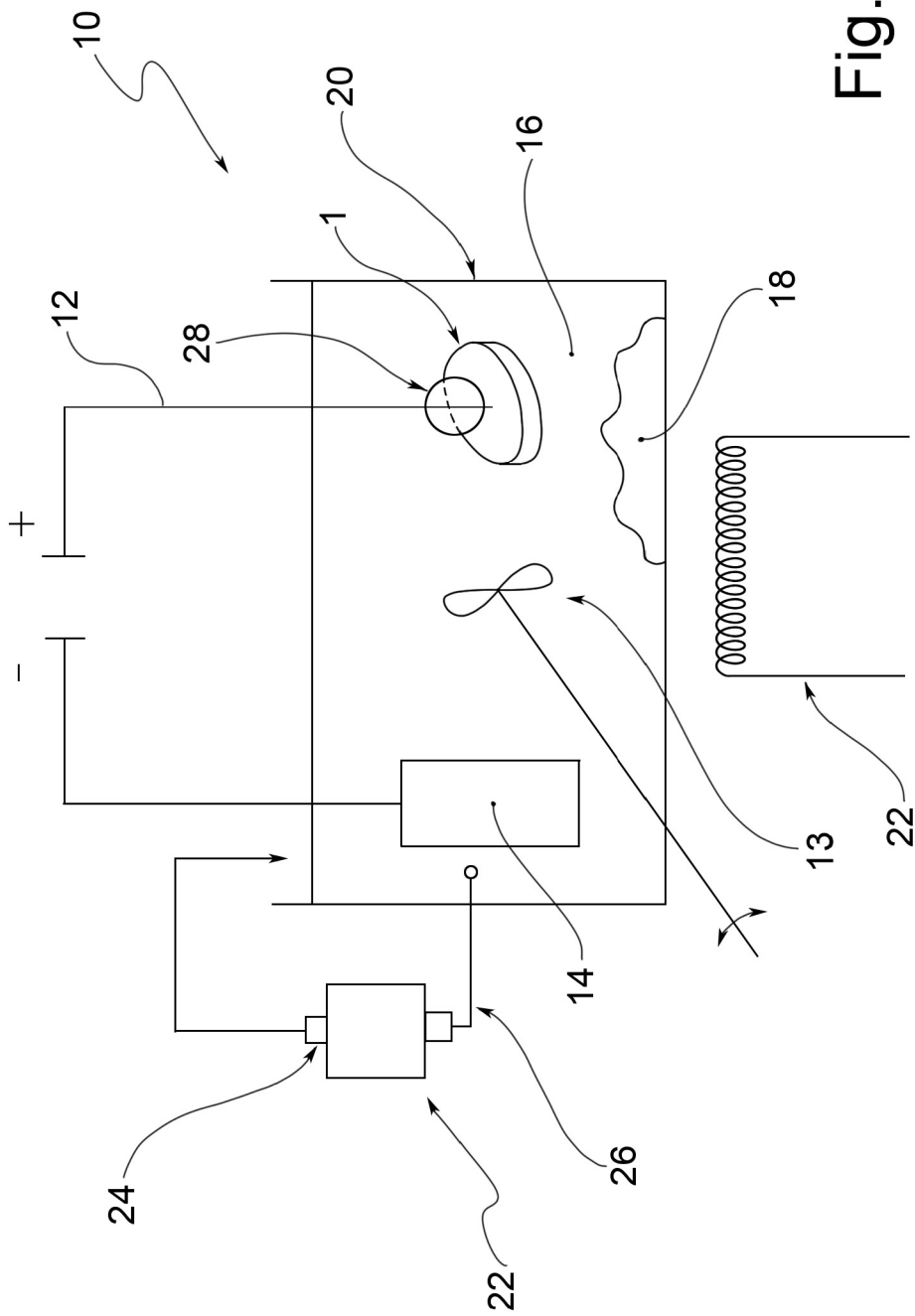


Fig.2

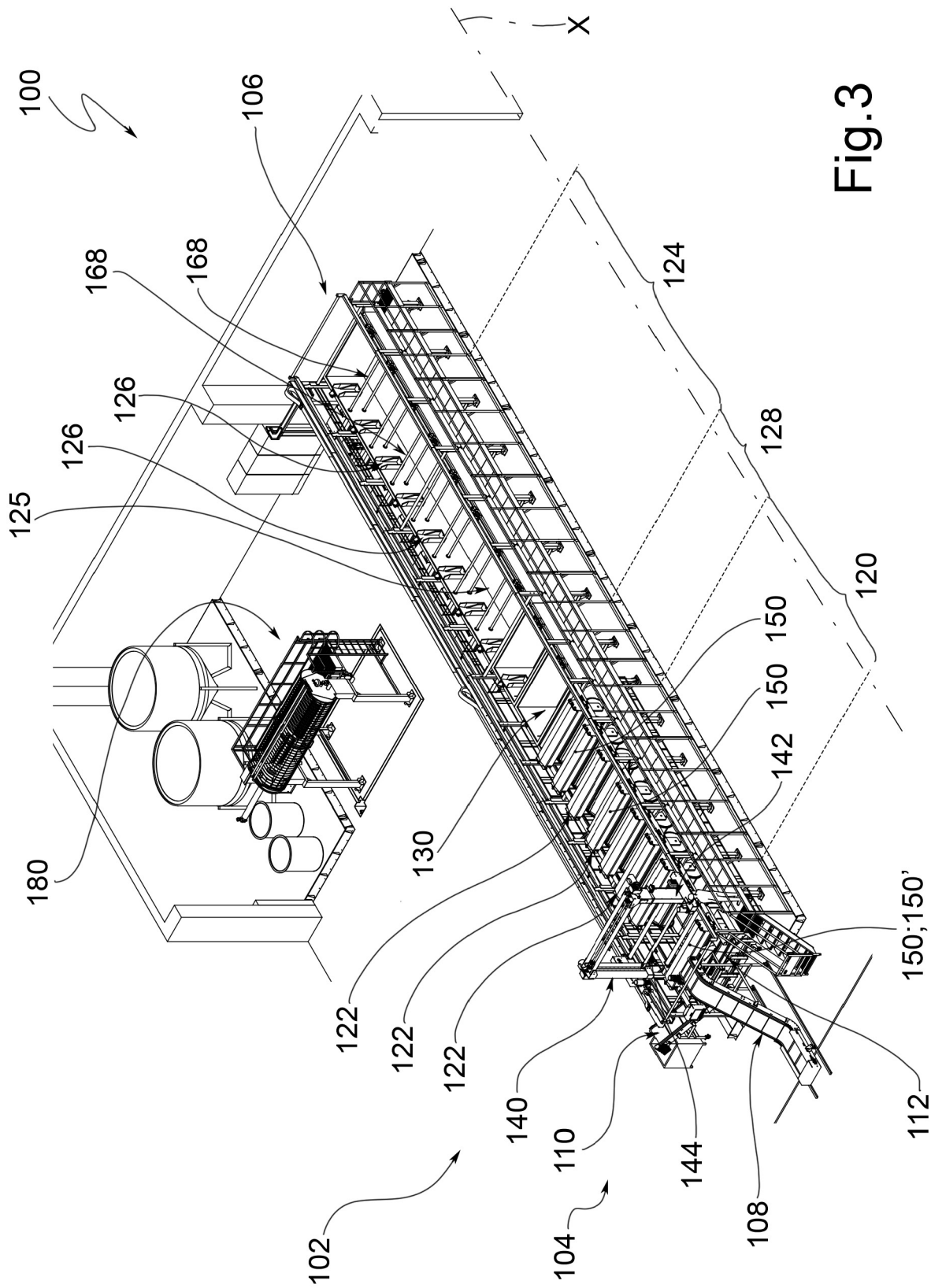


Fig.3

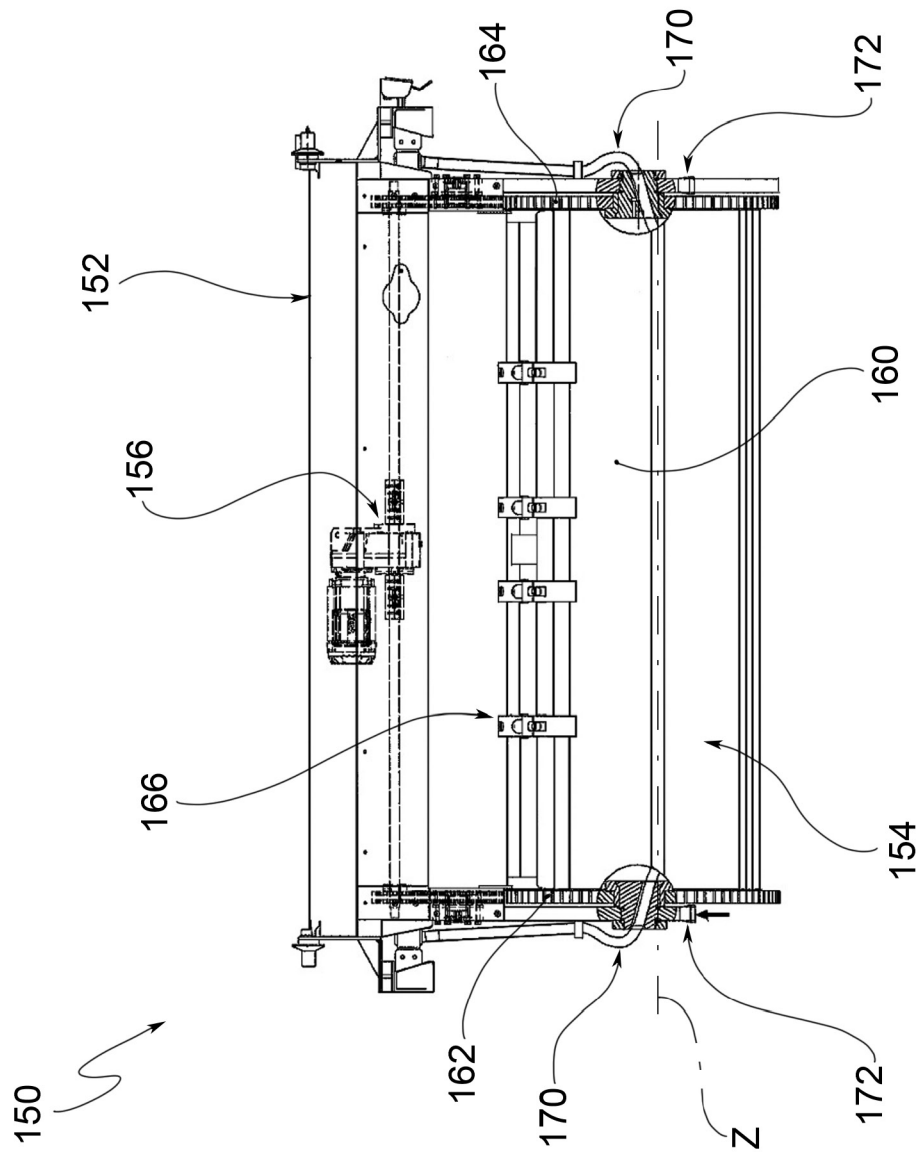


Fig. 4a

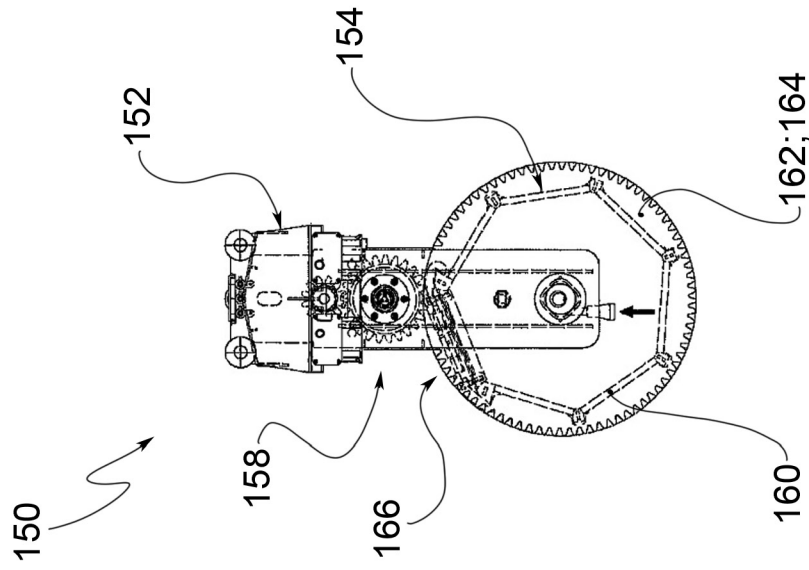


Fig. 4b



EUROPEAN SEARCH REPORT

Application Number

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The present search report has been drawn up for all claims			
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