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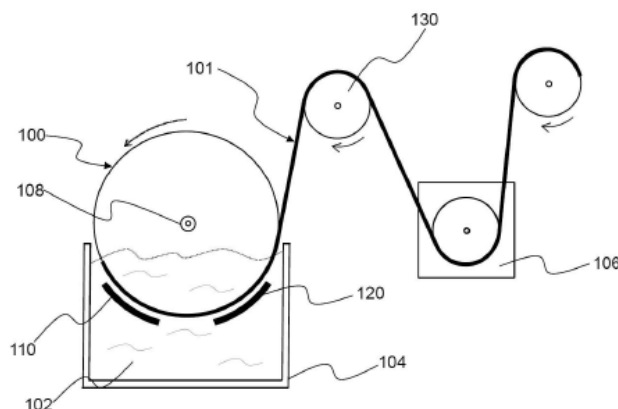
(54) Title of Invention: Method for manufacturing electrolytic copper foil for current collector
of secondary battery

(57) ABSTRACT

The present invention relates to a method of manufacturing an electrolytic copper foil for a current collector of a secondary battery, comprising: (a) a process of preparing a reaction tank in which a negative electrode (or cathode) rotary drum and one or more positive electrode (or anode) plates facing the cathode rotary drum are provided, and an electrolyte including copper sulfate and water mixed therein is filled; (b) a process of rotating the cathode rotary drum while applying electricity to both of the cathode rotary drum and the anode plates in order to precipitate copper on the surface of the cathode rotary drum; and (c) a process of continuously withdrawing the precipitated copper from the reaction tank, wherein fine embosses in such a structure that a distance V_1 between grooves of the embosses is larger than a depth V_2 of the groove, are formed on the surface of the cathode rotary drum, and the anode plate has a structure corresponding to the a part of the outer peripheral surface shape of the cathode rotary drum.

[Representative Drawing]

FIG. 1



CLAIMS

1. A method of manufacturing an electrolytic copper foil for a current collector of a secondary battery, comprising:

(a) a process of preparing a reaction tank in which a negative electrode (or cathode) rotary drum and one or more positive electrode (or anode) plates positioned to face the cathode rotary drum are provided, and an electrolyte including copper sulfate and water mixed therein is filled;

(b) a process of rotating the cathode rotary drum while applying electricity to both of the cathode rotary drum and the anode plates in order to precipitate copper on the surface of the cathode rotary drum; and

(c) a process of continuously withdrawing the precipitated copper from the reaction tank,

wherein fine embosses in such a structure that a distance V_1 between grooves of the embosses is larger than a depth V_2 of the groove are formed on the surface of the cathode rotary drum, and

the anode plate has a structure corresponding to a part of the outer peripheral surface shape of the cathode rotary drum.

2. The method according to claim 1, wherein the electrolyte is filled in the reaction tank to a height at which a part of the cathode rotary drum is exposed.

3. The method according to claim 2, wherein the electrolyte is filled in the reaction tank to a height at which 1/4 to 2/3 of the cathode rotary drum is exposed.

4. The method according to claim 1, wherein the anode plate is formed in a length of 20 to 100 degrees about a rotational shaft of the cathode rotary drum.

5. The method according to claim 1, wherein the anode plate comprises a first anode plate positioned opposite to one side of the cathode rotary drum and a second anode plate positioned opposite to the one side of the cathode rotary drum.

6. The method according to claim 5, wherein a reaction for generating a copper nucleus occurs at an outer surface portion of the cathode rotary drum facing the first anode plate, and a process of growing copper elements proceeds around the copper nucleus at the outer surface portion of the cathode rotary drum facing the second anode plate.

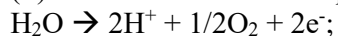
7. The method according to claim 1, wherein the cathode rotary drum is made of titanium or stainless steel material, while the anode plate is made of lead or a dimension safety electrode (DSA).

8. The method according to claim 1, wherein the above process (b) includes the copper precipitated by the following reaction:

(i) a reaction of the cathode rotary drum;



(ii) a reaction of the anode plate;



(iii) the entire reaction;



9. The method according to claim 1, wherein, in the process (b), an additive for leveling and glossing of the precipitated copper is further added.
10. The method according to claim 1, further comprising a process of coating the copper foil with chromium after the process (c).
11. The method according to claim 1, wherein the distance V_1 between grooves of the fine embosses has a size of 110 to 400% of the depth V_2 of the groove.
12. The method according to claim 1, wherein the depth V_2 of the groove of each of the fine embosses is in the range of 3 to 15 μm .
13. The method according to claim 12, wherein the depth V_2 of the groove of each of the fine embosses is in the range of 5 to 10 μm .
14. The method according to claim 1, wherein an inner angle of the groove of each of the fine embosses is more than 90 to less than 160 $^\circ$.
15. A current collector for a secondary battery manufactured by the method according to any one of claims 1 to 14.
16. The current collector according to claim 15, wherein fine embosses having such a structure that a distance F_1 between ridges of the fine embosses is larger than a depth V_2 of the groove are formed on either or both sides of the current collector.
17. An electrode for a secondary battery, comprising the current collector for a secondary battery according to claim 15 and an electrode material mixture containing an electrode active material applied thereto.
18. A secondary battery, comprising the electrode for a secondary battery according to claim 17.

DESCRIPTION

Technical Field

- [0001] The present invention relates to a method of manufacturing an electrolytic copper foil for a current collector of a secondary battery, more specifically, comprising: (a) a process of preparing a reaction tank in which a negative electrode (or cathode) rotary drum and one or more positive electrode (or anode) plates positioned to face the cathode rotary drum are provided, and an electrolyte including copper sulfate and water mixed therein is filled; (b) a process of rotating the cathode rotary drum while applying electricity to both of the cathode rotary drum and the anode plates in order to precipitate copper on the surface of the cathode rotary drum; and (c) a process of continuously withdrawing the precipitated copper from the reaction tank, wherein fine embosses in a structure, of which a distance V_1 between grooves of the embosses is larger than a depth V_2 of the groove, are formed on the surface of the cathode rotary drum, and the anode plate has a structure corresponding to a part of the outer peripheral surface shape of the cathode rotary drum.

Background of Art

- [0002] With an increase in the technical development and demand for mobile equipment, the demand for secondary batteries as an energy source has increased dramatically, and among such secondary batteries, a lithium secondary battery having a high energy density and voltage is commercially available and widely used.
- [0003] The lithium secondary battery generally consists of a positive electrode (or anode), a negative electrode (or cathode), a separator and a non-aqueous liquid electrolyte. The anode is formed of a current collector (hereinafter, "collector") with an anode active material layer applied thereto while the cathode is formed of another collector with a cathode active material layer applied thereto. Particularly, the anode is fabricated by applying an anode material mixture including an anode active material, a conductive material and a binder to an anode collector, drying the coated collector, rolling the same if needed, and then cutting the product into a desired shape. Similarly, the cathode is fabricated by applying a cathode material mixture including a cathode active material, a conductive material and a binder to a cathode collector, drying the coated collector, rolling the same if needed, and then cutting the product into a desired shape. The anode material mixture and the cathode material mixture may be each paste phase containing a dispersion medium, is each applied to either or both sides of the collector.
- [0004] In regard to the lithium secondary battery, an electrolytic copper foil is mainly used as a material for the cathode collector. Such electrolytic copper foil is manufactured by introducing an electrolyte comprising copper sulfate as a main component into a reaction tank that consists of a rotatable cylindrical cathode drum and an anode material refracted to correspond to an outer peripheral surface shape of a cathode material; electrodeposition of copper on the drum while rotating the same to precipitate the copper; continuously peeling the precipitated copper in a thickness of 3 to 500 μm and then winding the same. In general, a side transferred with the shape of an outer peripheral surface of a cylindrical cathode drum is smooth whereas the opposed side failed to transfer the growth of copper on the surface and becomes a roughened surface having irregular curves. Therefore, the roughened surface may be flattened by any post-treatment such as rolling or may be processed to have regular curves.
- [0005] On the other hand, the active material on the collector may be some deviated due to deterioration or swelling of the secondary battery, or external impact. Specifically, adhesion of the active material applied to the surface of the collector may be weakened by physical forces such as external impact as well as deterioration or swelling of the secondary battery, and further a gap occurs at a contact surface between the collector and the active material. As a result, the gap between the active material and the collector may reduce a surface area on which current and electrons move, to cause a phenomenon that the current and electrons are concentrated to a specific point, hence increasing internal resistance of the cathode.
- [0006] In this regard, in order to improve adhesiveness of the collector, some prior art proposed a technique of forming fine embosses on the surface of the collector by a process such as sand blasting or etching to enhance adhesive force, however, such fine embosses formed by the above process have considerably irregular sizes, which in turn cause a disadvantage in that a density of the applied active material is not uniform.
- [0007] Accordingly, a new technology capable of forming fine embosses in a uniform size while having excellent adhesion to active materials is now needed.

Detailed Description of Invention

Technical Problem to be Solved

- [0008] Therefore, the present invention is directed to solve the problems of prior art as described above, as well as technical problems which have been requested from the prior art.
- [0009] At the end of extensive and intensive researches and various experiments, as described below, the present inventors have developed a method of manufacturing electrolytic copper foil for a collector in a secondary battery, which has fine embosses formed in a predetermined size and in such a structure that a distance V_1 between grooves is larger than a depth V_2 of the groove. Further, it was confirmed that, when using the electrolytic copper foil manufactured by the above method, adhesion to a cathode material mixture is improved to prevent deterioration and swelling of a battery, efficiency of the battery manufacturing process is increased to achieve desired effects, thereby completing the present invention.

Technical Solution

- [0010] The manufacturing method according to the present invention to accomplish the above object is a method of manufacturing an electrolytic copper foil for a collector of a secondary battery, which includes:
- [0011] (a) a process of preparing a reaction tank in which a cathode rotary drum and one or more anode plates positioned to face the cathode rotary drum are provided, and an electrolyte including copper sulfate and water mixed therein is filled;
- [0012] (b) a process of rotating the cathode rotary drum while applying electricity to both of the cathode rotary drum and the anode plates in order to precipitate copper on the surface of the cathode rotary drum; and
- [0013] (c) a process of continuously withdrawing the precipitated copper from the reaction tank,
- [0014] wherein
- [0015] fine embosses in such a structure that a distance V_1 between grooves of the embosses is larger than a depth V_2 of the groove are formed on the surface of the cathode rotary drum, and the anode plate has a structure corresponding to a part of the outer peripheral surface shape of the cathode rotary drum.
- [0016] That is, fine embosses are formed on the surface of the cathode rotary drum according to the present invention to induce precipitation of copper and thus correspond to a shape of the surface of the fine emboss, thereby enabling production of an electrolytic copper foil having uniform fine emboss. As a result, the electrolytic copper foil having fine embosses formed therein in such a structure that a distance V_1 between grooves of the embosses is larger than a depth V_2 of the groove may have relatively smooth surface roughness and enable production of thin collectors, thereby reducing a volume of the battery.
- [0017] The electrolyte in the present invention may be filled in a reaction tank to a height at which a part of the cathode rotary drum is exposed, in order to maximize a contact area between the cathode rotary drum and the anode plate and in consideration of a concentration of copper ions in the electrolyte. Specifically, the electrolyte may be filled in the reaction tank to a height at which 1/4 to 2/3 of the cathode rotary drum is exposed based on a diameter of the cathode rotary drum.

- [0018] The anode plate may be formed in different lengths and in a structure corresponding to a part of the outer peripheral surface shape of the cathode rotary drum, specifically, in a length of 20 to 100 degrees to a rotational axis of the cathode rotary drum.
- [0019] Further, in order to control the growth of copper precipitated on the surface of the cathode rotary drum, two or more anode plates may be separated and mounted at a predetermined interval. Specifically, the anode plate mounted herein may be divided into a first anode plate positioned opposite to one side of the cathode rotary drum and a second anode plate positioned opposite to the one side of the cathode rotary drum.
- [0020] A reaction of generating copper nuclei occurs on an outer surface portion of the cathode rotary drum facing the first anode plate, while a process of growing copper elements around the copper nuclei may take place on the outer surface portion of the cathode rotary drum facing the second anode plate.
- [0021] That is, the anode plates may be separated toward one side and the opposed side to form a predetermined interval, and a copper growth rate is stalled at the interval. Consequently, separately assembling the anode plates has an advantage in that a growth rate of copper precipitated on the surface of the cathode rotary drum may be controlled to thus adjust a thickness of copper foil and surface roughness.
- [0022] Meanwhile, the cathode rotary drum may be selected in consideration of materials with high intensity, corrosion resistance to an electrolyte or the like, and easy maintenance, so as to enable continuous use over a long period of time. Specifically, the materials may be titanium or stainless steel, however, not particularly limited thereto. Further, the anode plate may be any general anode material for electroplating, which is known in the art, such as lead or dimension safety electrode (DSA), however, not particularly limited thereto.
- [0023] In the present invention, the above process (b) may precipitate the copper by the following reaction:
- [0024] (i) a reaction of the cathode rotary drum;
- [0025] $\text{CuSO}_4 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{Cu} + \text{H}_2\text{SO}_4$
- [0026] (ii) a reaction of the anode plate;
- [0027] $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 1/2\text{O}_2 + 2\text{e}^-$;
- [0028] (iii) the entire reaction;
- [0029] $\text{CuSO}_4 + \text{H}_2\text{O} \rightarrow \text{Cu} + \text{H}_2\text{SO}_4 + 1/2\text{O}_2$.
- [0030] Further, in the process (b), an additive for leveling and glossing of the precipitated copper may further be added.
- [0031] The method of the present invention may further comprise a process of coating the copper foil with chromium after the process (c).
- [0032] The distance V_1 between grooves of the fine embosses may have a size of 110 to 400% of the depth V_2 of the groove, and the depth V_2 of the groove of each of the fine embosses may be formed in the range of 3 to 15 μm . Specifically, the depth V_2 of the groove of each of the fine embosses may be in the range of 5 to 10 μm , more specifically, about 8 μm .
- [0033] If the distance V_1 between grooves of the fine embosses and the depth V_2 of the groove is too small, it is difficult to form fine embosses which, in turn, may cause a difficulty in dispersion of stress at volume expansion of an electrode active material. On the contrary, if the surface roughness is too large, it may occur a problem of deteriorating stress dispersion and

alleviation effects of the electrode active material within the emboss formed in a large size, which is not preferable.

- [0034] Further, an inner angle of the groove of each of the fine embosses may be more than 90 to less than 160 °.
- [0035] Accordingly, the fine embosses formed in a desired size at a predetermined interval may improve adhesiveness of the electrolytic copper foil, and may enable the applied electrode active material to have uniform density distribution. As a result, it is possible to prevent release of a cathode material mixture due to deterioration or swelling of a secondary battery or external impact, and further to inhibit internal resistance due to a gap. Further, unsafe (or instable) behavior of the electrode due to a difference in density distributions of active materials may be prevented in advance.
- [0036] Further, the present invention may provide a current collector for a secondary battery according to the above manufacturing method.
- [0037] With regard to the current collector for a secondary battery, fine embosses having such a structure that a distance F_1 between ridges of the fine embosses is larger than a depth V_2 of the groove may be formed on either or both sides of the current collector. Therefore, fine embosses having relatively smooth slopes are formed in the above collector, and no empty space is formed on a surface corresponding to the fine emboss when applying an active material, so that a density distribution of the active material on the collector is evenly maintained to thus enhance safety.
- [0038] The collector for a secondary battery according to the present invention may provide an electrode for a secondary battery, which is prepared by applying an electrode material mixture containing an electrode active material to a surface of the collector for a secondary battery as described above, specifically, the above electrode for a secondary battery may be a cathode.
- [0039] The present invention may further provide a secondary battery, comprising the electrode for a secondary battery as described above, specifically, the secondary battery may be a lithium secondary battery.

Effects of Invention

- [0040] As described above, the manufacturing method according to the present invention includes forming fine embosses having such a structure that a distance V_1 between grooves of the embosses is larger than a depth V_2 of the groove in a cathode rotary drum, and separately mounting a first anode plate and a second anode plate positioned opposite to one side of the cathode rotary drum, so as to produce an electrolytic copper foil wherein not only fine embosses having uniform size and intervals, but also a fine emboss part with relatively smooth slopes are formed on the surface of the copper foil to thus improve adhesiveness and safety, whereby a secondary battery having a collector capable of preventing release of the active material and internal resistance can be provided.

Brief Description of Drawings

- [0041] FIG. 1 is a schematic view illustrating the configuration of a process for manufacturing an electrolytic copper foil according to one embodiment of the present invention.

FIG. 2 is a schematic view illustrating a reaction tank provided with a cathode rotary drum, a first anode plate and a second anode plate according to another embodiment of the present invention.

FIG. 3 is a schematic view illustrating the cathode rotary drum according to the present invention.

FIG. 4 is an enlarged view illustrating 'a' portion in FIG. 4.

FIG. 5 is a schematic view illustrating the surface of the electrolytic copper foil according to the present invention.

Preferred Embodiment for Carrying Out Invention

- [0042] Hereinafter, the present invention will be described with reference to the accompanying drawings according to preferred embodiments of the present invention. However, the above description is given for more easily understanding the present invention and the scope of the present invention is duly not limited thereto.
- [0043] FIG. 1 is a view schematically illustrating the configuration of the manufacturing process of electrolytic copper foil 101 according to the present invention.
- [0044] Referring to FIG. 1, the cathode rotary drum 100 is inserted in a reaction tank 104 that is continuously supplied with an electrolyte 102 consisting of sulfuric acid and copper ions from an electrolyte feed tank (not shown).
- [0045] The cathode rotary drum 100 includes a rotational shaft 108 passing through a center portion, which is fixed on a bearing (not shown) located on both sides of a top of the reaction tank 104, wherein the electrolyte 102 consisting of sulfuric acid and copper ions is filled in the reaction tank 104 to a height at which a portion of the cathode rotary drum is exposed, specifically, 1/3 of the cathode rotary drum based on a diameter thereof is exposed (expressed by dashed lines). Further, a first anode plate 110 and a second anode plate 120 are installed in the reaction tank such that the anode plates are positioned opposite to one side of the cathode rotary drum 100 and spaced at a predetermined gap to correspond to the shape of an outer peripheral surface of the cathode rotary drum. The first anode plate 110 and the second anode plate 120 are each spaced and positioned at predetermined intervals, respectively.
- [0046] The cathode rotary drum 100 rotates to precipitate copper on an outer surface area of the cathode rotary drum 100 facing the first anode plate 110 in a state that a portion of the drum is exposed to the electrolyte 102, and enables the growth of copper ions around copper nuclei on the outer surface area of the cathode rotary drum 100 facing the second anode plate 120, so as to electro-deposit an electrolyte copper foil 101 in a thin film form on the surface of the cathode rotary drum 100, followed by rolling a rough side through a roller 130 to minimize curves and then transferring the product to a second reaction tank 106 containing a chromium salt solution.
- [0047] The second reaction tank 106 is filled with the chromium salt solution, the electrolyte copper foil 101 is impregnated in the chromium salt solution so that the surface of the copper foil is coated with chromium and a fine emboss part formed on the surface of the electrolyte copper foil is stably fixed.
- [0048] The roller 130 is possibly installed in plural in order to conduct electrodeposition of the electrolytic copper foil 101 continuously, and may further be provided with the configuration

such as a heat-resistant water bath (not shown) to prevent spreading of the electrolytic copper foil 101 on each roller, an anti-rust water bath (not shown) to prevent oxidation of the electrolytic copper foil 101, a silane water bath (not shown) coated with a silane coupling agent to ensure adhesion of the electrolytic copper foil, etc.

- [0049] FIG. 2 schematically illustrates the configuration of the reaction tank 104 comprising the cathode rotary drum 100, the first anode plate 210 and the second anode plate 220.
- [0050] Referring to FIG. 2, the first anode plate 210 is formed in a length corresponding to an angle (Θ_1) about the rotational shaft 108 passing through the cathode rotary drum 100, while the second anode plate 220 is formed in a length corresponding to another angle (Θ_2) about the above rotational shaft.
- [0051] Therefore, the first anode plate 210 and the second anode plate 220 have a structure that controls a copper growth rate as much as a distance spaced between both of the anode plates, specifically, a process of precipitating and growing copper may be controlled depending on the lengths of the anode plates to thus adjust the thickness and surface roughness of the electrolytic copper foil.
- [0052] FIG. 3 schematically illustrates the cathode rotary drum 100 according to the present invention, while FIG. 4 shows an enlarged cross-section of 'a' part in FIG. 4.
- [0053] Referring these figures, the cathode rotary drum 100 made of titanium or stainless steel has a cylindrical shape, wherein fine embosses 300a are formed over the entire surface around a cylindrical circumference except for the surfaces of both ends.
- [0054] Such fine embosses 300 include grooves 301 and ridges, which are uniformly and repeatedly formed, wherein a distance V_1 between the grooves may have a size of 110 to 400% of a depth V_2 of the groove, and the V_2 of the groove may be formed in the range of 3 to 15 μm . Further, an angle (Θ_3) of the groove in the fine emboss exceeds 90°, and may form a low slope. The emboss with the low slope may have uniformity in error range so that a density distribution of the applied active material can be uniform on the collector.
- [0055] FIG. 5 schematically illustrates an enlarged surface of the electrolytic copper foil 101 according to the present invention.
- [0056] Referring to FIG. 5, the electrolytic copper foil 101 is formed in such a structure that a distance F_1 between ridges 401 is larger than a depth V_2 of the groove 402 in a surface transferred from the cathode rotary drum, and is provided with embosses 400 corresponding to the fine embosses 300a formed around a part of the outer peripheral surface of the cathode rotary drum 300. As such, the opposite side of the surface having the embosses 400, that is, a rough surface (expressed by dashed lines) may be relatively smoothly processed. Alternatively, it is also possible to form natural emboss without processing the rough surface, thereby enabling application of the active material at both sides of the collector.
- [0057] As described above, the present invention has been described with reference to the accompanying drawings according to the embodiments of the present invention, however, those skilled in the art to which the present invention pertains, would possibly perform various applications and modifications based on the above description within the scope of the present invention.

Drawings
FIG. 1

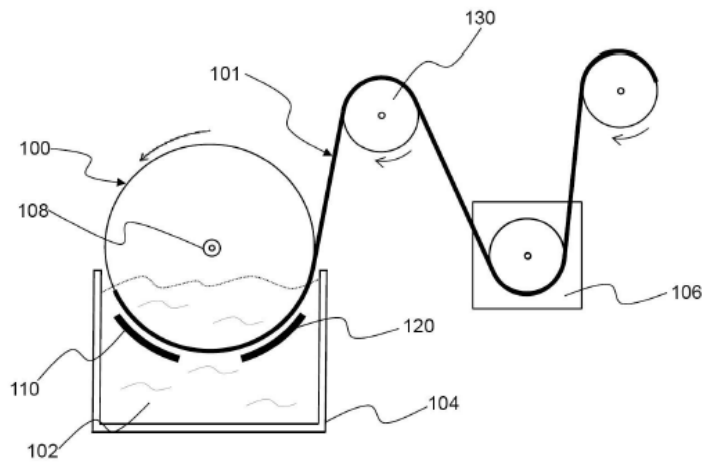


FIG. 2

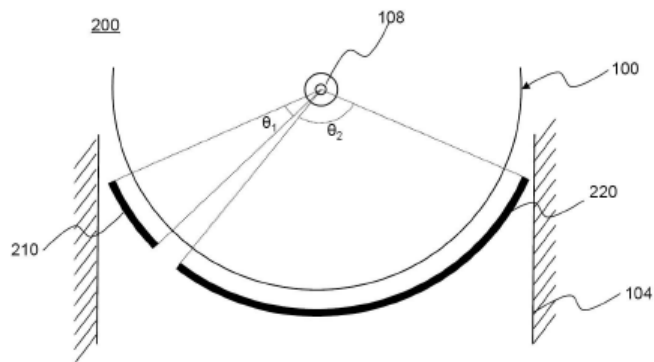


FIG. 3

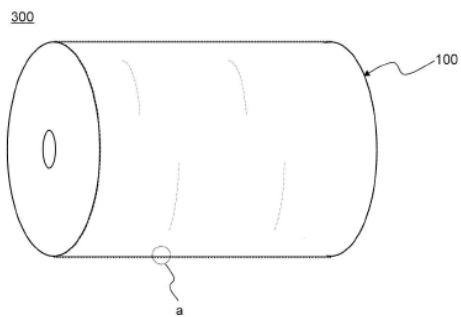


FIG. 4

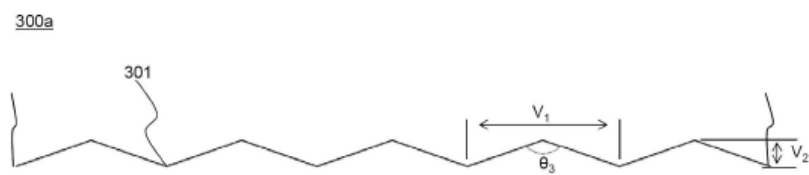
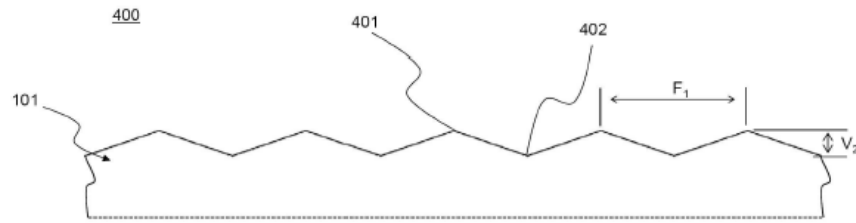


FIG. 5





TRANSLATOR'S CERTIFICATE OF TRANSLATION

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Questel Project Number: FRPC2430040UT-LZ
Date: August 1, 2024

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I, Kyung-ah, OH, a translator fluent in the Korean and English languages, on behalf of Questel, do solemnly and sincerely declare that the following is, to the best of my knowledge and belief, a true and correct translation of the document(s) listed below in a form that best reflects the intention and meaning of the original text.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I further declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

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Name