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W. HOOPES

ELECTROLYTICALLY REFINED ALUMINUM AND ARTICLES MADE THEREFROM

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Fig. 1

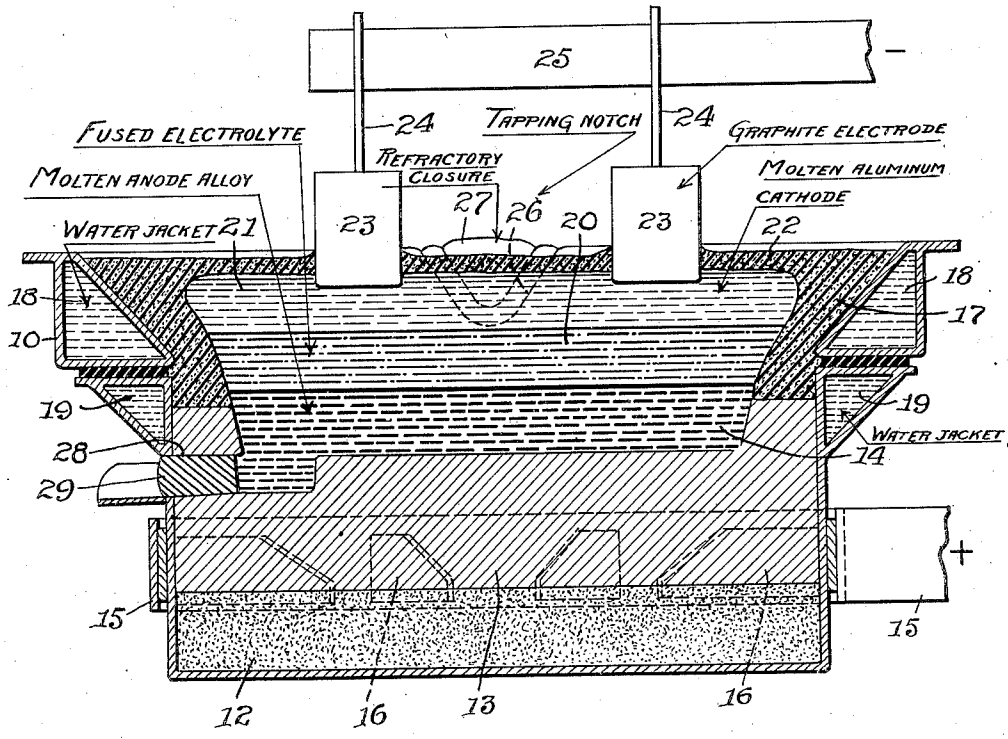
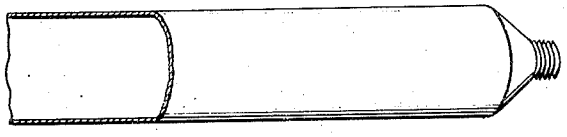


Fig. 2



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UNITED STATES PATENT OFFICE.

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ELECTROLYTICALLY-REFINED ALUMINUM AND ARTICLES MADE THEREFROM.

Application filed December 21, 1922. Serial No. 608,282.

To all whom it may concern:

Be it known that I, WILLIAM HOOPES, a citizen of the United States of America, residing at Pittsburgh, in the county of Allegheny and State of Pennsylvania, have invented certain new and useful Improvements in Electrolytically-Refined Aluminum and Articles Made Therefrom, of which the following is a full, clear, and exact description.

This invention relates to metallic aluminum, and consists chiefly in the provision of commercial electrolytically-refined aluminum having certain characteristics or properties fitting it for various uses to which metal produced heretofore by the well know Hall (or Heroult) process is not well adapted, if at all. Among the characteristics referred to, the most important, from some standpoints, is the high purity of my metal, which has a purity ranging from about 99.85 per cent to 99.98+ per cent, and even higher, with a correspondingly low impurity content consisting chiefly, in most cases, of iron, copper, and silicon (or one or more of these elements) and possibly traces of other substances. Other desirable properties of my metal are its extreme softness, ductility, and malleability. Of the base metals commonly used for articles of manufacture, lead and tin are the softest and copper the most ductile. My metal is as ductile as electrolytically refined copper; its elongation, as measured on worked and annealed pieces by methods approved by the U. S. Bureau of Standards, being 57 to 60 per cent. In softness my metal exceeds all the base metals referred to except tin and lead, and is notably softer than the purest aluminum produced by the Hall process. Not only is my metal highly malleable and more ductile than tin, but it is almost twice as strong, and hence possesses an exceptional combination of physical properties. Another striking property is its high resistance to attack by dilute acids. For example, specimens of my electrolytically refined aluminum, in the form of very thin sheets, have been left immersed at room temperature for several hours in a solution composed of concentrated hydrochloric acid 5 parts (by volume) and water 95 parts. After five weeks they were still bright and showed no appreciable corrosion. Under the same conditions the best grade of aluminum obtained by the Hall process is almost completely dissolved in a few days. To produce a similar result with my metal required six months or more.

Aluminum possessing in a high degree the above qualities or properties can be produced commercially by the electrothermal reducing and electrolytic refining method described and claimed in the copending application of myself, Francis C. Frary and Junius D. Edwards, Serial No. 608,283, filed December 21, 1922. It can also be made at a commercially low cost in the following manner.

The method last mentioned is an electrolytic process, employing a molten anode composed of a relatively dense aluminum-alloy, a cathode composed of pure aluminum in the molten state, and a molten fluorid bath or electrolyte of intermediate density. These bodies are gravitatively arranged in layers in a suitable electrolytic cell or vessel, with the relatively heavy anode alloy at the bottom, the lighter bath floating on the anode, and the still lighter cathode floating on the bath. When unidirectional current is passed from one metallic layer to the other through the electrolyte, aluminum is dissolved from the anode and deposited on the cathode.

In the accompanying drawing,

Fig. 1 shows in cross section a cell suitable for practicing the process outlined above; and

Fig. 2 is a perspective view, partly in longitudinal section, of a "collapsible tube" made of my electrolytically refined aluminum.

The cell illustrated in Fig. 1 is similar to that described in my copending application Serial No. 608,287, filed December 21, 1922, and comprises a steel shell preferably of cylindrical form, divided horizontally into electrically separated upper and lower sections 10, 11. In the latter is a layer 12 of re-

fractory heat-insulating material, as for example powdered bauxite, and on this layer is a bottom lining 13 composed of conducting carbon and formed with a bowl-like cavity or receptacle for the molten anode alloy 14. Current is led into the carbon bottom (from the positive terminal of a suitable source of current, not shown) by means of a positive busbar 15 connected to steel distributor plates 16 welded to the shell and embedded in said carbon bottom.

Extending upwardly from the carbon bottom 13 and covering the joint between the shell sections is a thermally and electrically insulating refractory lining 17, which may be frozen on the shell walls, as described in the copending application of myself, Junius D. Edwards and Basil T. Horsfield, Serial No. 608,289, filed December 21, 1922, by means of the encircling water-jackets 18, 19, which also aid in keeping the lining solid when the refining process is going on.

The fused bath or electrolyte, which floats on the anode alloy 14, is indicated at 20, and the molten aluminum cathode, floating on the bath, is indicated at 21. Above the latter is a thermally insulating refractory top crust 22, to diminish loss of heat by radiation from the open top of the cell and protect the molten pure aluminum layer from oxidation by contact with the air. This top crust may be composed of bath ingredients and can be produced in the way described in the copending application of myself and Francis C. Frary, Serial No. 608,286, filed December 21, 1922.

Current is led out of the molten aluminum cathode 21 by means of one or more electrodes 23, preferably composed of graphite, connected by rods 24 to a negative busbar 25 leading to the negative terminal of a source of current, not shown.

In the upper cell section is a tapping notch 26 (into which the side lining 17 extends) for tapping out the refined aluminum at appropriate intervals. At other times the notch is closed by a mass 27 of suitable refractory material, as for example bath material. In the lower cell section is a tapping hole 28 for withdrawal of residual or impoverished anode alloy from time to time. This hole may be closed by means of a plug of dense charcoal, 29. To start the refining process the molten anode alloy 14, the molten bath 20, and the molten cathode 21, can be deposited in succession in the cell, before or after the electrolyzing current is turned on. The effect of the flow of current is to dissolve aluminum from the anode alloy and deposit aluminum on the cathode; and, by the resistance losses in the bath or electrolyte and consequent liberation of heat, to keep the cell contents (anode, bath and cathode) adequately mobile.

The anode alloy is preferably of about the following composition: Aluminum (e. g., produced by the Hall process) and copper in the proportion of about 60:40, respectively, and silicon up to 10 per cent. Iron, though not an advantageous ingredient, may also be present up to about 10 per cent. An alloy of this composition is adequately mobile at temperatures above about 950° C. The electrolyte or bath is composed chiefly of fluorids, and the composition is preferably about as follows: Aluminum fluorid 33 per cent; sodium fluorid 30 per cent; barium fluorid 35 per cent; and alumina 2 per cent. The barium fluorid may be replaced, in whole or in part, by a suitable amount of strontium fluorid. For an extended discussion of anode alloys suitable for the present process, reference may be made to the copending application of myself, Francis C. Frary and Junius D. Edwards, Serial No. 608,284, filed December 21, 1922; and to the copending application of myself, Francis C. Frary and Junius D. Edwards, Serial No. 608,285, filed December 21, 1922, for a like discussion of electrolytes. Alumina is not a harmful ingredient of the bath. If the bath is saturated with alumina, however, more or less of the latter may freeze out on the side lining, and if this continues (as may be the case where the process is performed under conditions permitting accumulation of alumina in the bath, as for example in a plant where the Hall process is carried on), the cell lining may thicken so much as to make the available capacity of the cell too small for efficient operation, and might even choke up the cell entirely. Accordingly it may be necessary or desirable to remove alumina from the bath from time to time. This may be done by any of the methods described in the copending application of myself and Francis C. Frary, above referred to; as for example by breaking out more or less of the side lining and allowing a new lining to form, or by removing a portion of the bath and adding fresh bath free from alumina.

The cathode employed in starting is preferably the best grade of aluminum obtainable. As the operation proceeds, with the deposition of pure aluminum on the cathode, the relative amount of impurity on the cathode diminishes, so that after a few withdrawals the cathode metal will be found to be of the high purity desired.

The voltage employed should be no higher than that necessary to keep the cell contents in the necessary molten or mobile condition. For a cell of the type described, having an active anode area of about 14.5 square feet a voltage of 6 to 7 volts is ordinarily sufficient, but it may of course be higher. The current density with the anode area mentioned may be between 900 and 1400 amperes per square foot, with a preferred current density of approximately 1200 am-

peres per square foot of active anode area. As the refining process goes on, the removal of aluminum from the anode alloy decreases the volume of the latter and at the same time the volume of the cathode is increased by the aluminum deposited thereon, while the bath remains substantially constant in thickness, though descending slowly in the cell. When the desired amount of aluminum has been deposited a portion of the cathode metal is drawn off through the tapping notch and fresh anode alloy is supplied in any way which will not contaminate the pure aluminum layer, as for example by means of a carbon funnel (not shown) let down into the anode layer from the top. The withdrawal of cathode metal and addition of anode alloy may be effected simultaneously, the fresh anode alloy being supplied in sufficient amount to raise the lower surface of the remaining cathode metal well to its original position. Of course no current is allowed to flow through the cell during these operations. In the course of time, impurities left behind in the anode may accumulate therein to such an extent as to permit deposition thereof on the cathode in amount sufficient to seriously affect the purity of the latter. In such case more or less of the alloy may be withdrawn through the tapping hole in the lower section of the cell and fresh alloy may then be supplied to take its place.

With the above described process, carried out on a large scale in actual commercial operation, I am able to produce electrolytically refined aluminum having the striking properties or qualities mentioned at the beginning of this specification. As there stated, these qualities make the metal especially suitable for various purposes. For example, its high resistance to attack by acids adapts it for use in the form of pipes, vessels, and other devices for handling products of an acid nature in chemical and allied arts. Similarly, its exceptional ductility and malleability are highly advantageous for articles requiring such properties in their manufacture, as for example wires and sheets. Thus the metal described may be readily rolled or hammered to a thin foil or drawn out in the form of thin wire. Its remarkable softness, combined with other properties mentioned, especially its relatively great strength, gives it an important advantage for making "collapsible tubes", and it is now extensively used for that purpose; whereas similar tubes made of the best grade of aluminum heretofore obtainable have not been pliable enough to be rolled up easily by the fingers as the tube contents are expelled. On the other hand collapsible tubes made of tin are weak and hence apt to break if the contents are stiff or insufficiently plastic. Methods of making wires by drawing, sheets by rolling or hammering, and tubes by drawing or extruding are so well known that it is deemed unnecessary to illustrate or describe such methods, or, generally, the articles themselves. A collapsible tube, however, is shown in Fig. 2, partly in section. For the purpose of covering, as broadly as possible, articles made by methods involving extruding, drawing, hammering, rolling, stamping, and the like (wherein ductility and malleability are important), I have in the appended claims described such articles as "extended from" a smaller body.

Among other characteristics, properties or qualities of my electrolytically refined aluminum, mention may be made of its melting point, which is approximately 659° .5±0.3 C. Measured at 20° C. the specific electrical resistivity of the annealed metal is in the neighborhood of 2.7 microhms per centimeter cube, or lower. In color my metal is distinctly silvery with notably less of the bluish or grayish appearance characteristic of ordinary aluminum. It solidifies with a mirror-like lustre and retains its lustre for remarkably long periods of time under ordinary atmospheric conditions.

It is to be understood that the appended claims are intended to cover, broadly, electrolytically refined aluminum and articles made of the same, having the properties, qualities, or characteristics set forth in the claims, whether the metal is produced by the herein described or any other method of electrolytic refining.

I claim—

1. As a new commercial product, substantially pure electrolytically refined metallic aluminum, softer than all other base metals except tin and lead, in ductility equal to copper and exceeding tin in tensile strength, having an aluminum content of at least 99.8 per cent, and capable of being immersed in dilute hydrochloric acid for long periods of time without material corrosion thereby.

2. As a new commercial product, substantially pure elctrolytically refined metallic aluminum, containing in the aggregate not more than about 0.15 per cent of iron, silicon and copper impurity, in softness second only to lead and tin among the base metals and having greater tensile strength than tin, and substantially unaffected by prolonged immersion in dilute hydrochloric acid.

3. As a new commercial product, substantially pure elctrolytically refined metallic aluminum, at least 99.9 per cent pure, containing in the aggregate not more than 0.1 per cent of iron, silicon and copper, and more ductile than copper and having greater tensile strength than tin.

4. An article of manufacture composed of

electrolytically refined metallic aluminum not less than about 99.85 per cent pure, capable of withstanding prolonged contact with dilute hydrochloric acid without material corrosion thereby.

5. An article of manufacture extended from a smaller body, composed of electrolytically refined metallic aluminum at least 99.8 per cent pure, equal to copper in ductility and possessing greater tensile strength than tin, and capable of withstanding prolonged contact with dilute hydrochloric acid without material corrosion thereby.

In testimony whereof I hereto affix my signature.

WILLIAM HOOPES.