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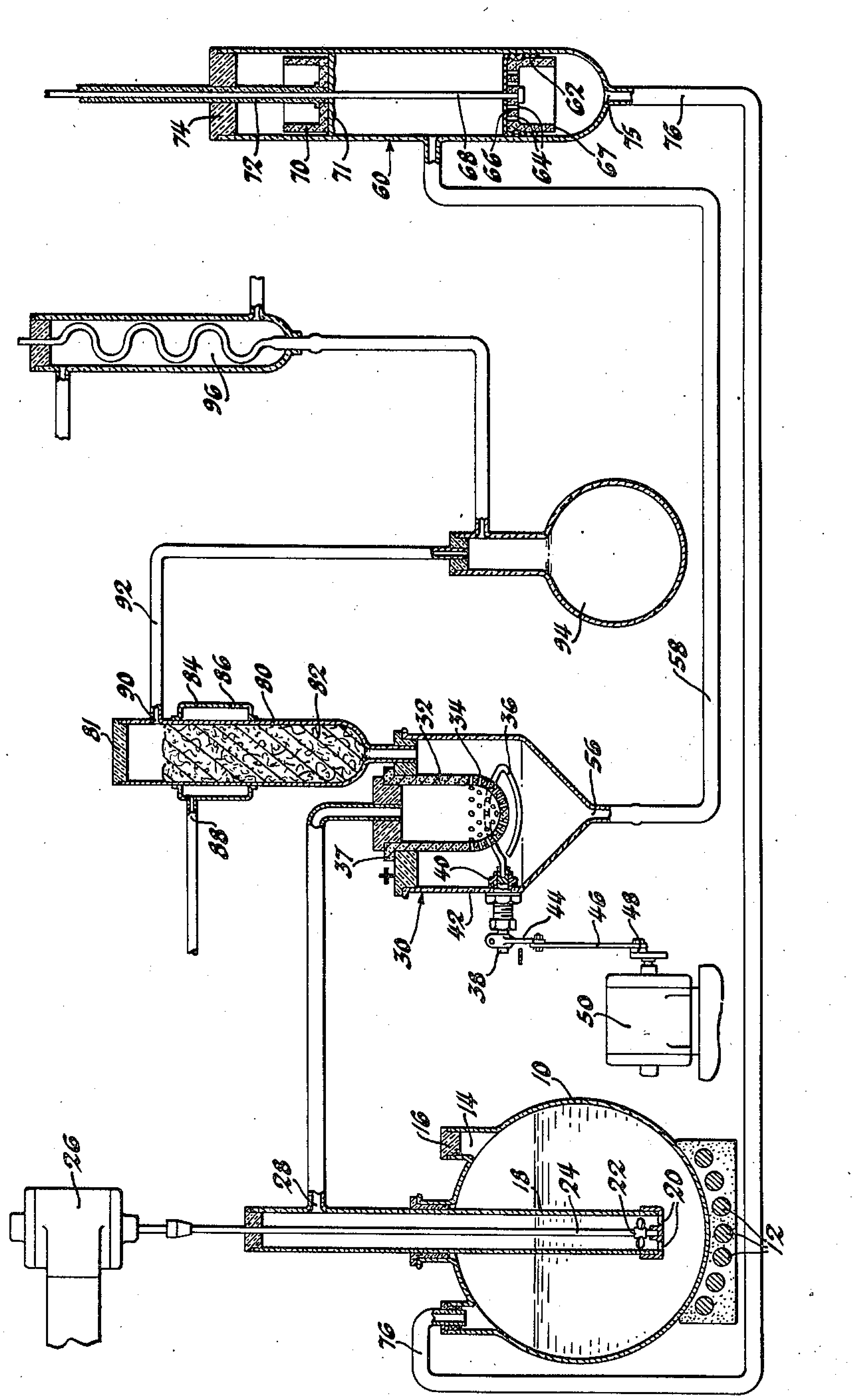

Inventors
Wheeler G. Lovell &
Nelson E. Phillips
By
Blackmore, Spencer & Flint
Attorneys

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ELECTROLYTIC REDUCTION OF ALUMINUM BROMIDE

Wheeler G. Lovell and Nelson E. Phillips, Detroit, Mich., assignors to General Motors Corporation, Detroit, Mich., a corporation of Delaware

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9 Claims. (Cl. 204—67)

This invention relates generally to the electrolytic reduction of compounds of aluminum to produce metallic aluminum. More specifically the invention has to do with the electrolytic reduction of a fused electrolyte containing aluminum bromide.

Among the objects of the invention are the following: to provide an improved method and apparatus for producing metallic aluminum, to provide a convenient and practical electrolytic method and apparatus for the production of aluminum that has more advantageous energy relations than present methods, to provide a process and apparatus for producing aluminum that reduces the cost as compared with present practice, to provide a practical and economical method and apparatus for producing aluminum of a high degree of purity; to provide improvements in a method and apparatus of producing substantially pure aluminum which makes it possible to utilize economically a wider variety of cheaper aluminum containing raw materials than present commercial processes; to provide improvements in a method and apparatus for recovering substantially pure aluminum as it is formed by the electrolytic reduction of the aluminum compound in the electrolyte; to provide improvements in anodes and cathodes, especially those for use in the electrolytic reduction of aluminum bromide. Other objects and advantages of the invention will become more apparent as the description proceeds. Reference is herewith made to the accompanying drawing forming a portion of this specification in which the figure illustrates somewhat diagrammatically one form of apparatus adapted to carry out the method in accordance with the invention.

General description

The device illustrated comprises a means for heating and continuously circulating through a generally closed system a fused electrolyte of suitable boiling point containing aluminum bromide, air and water being excluded from the system. The fused, non-aqueous electrolyte passes through an anode which directs the electrolyte in proper relation with respect to a vibratory cathode. The device is so constructed and controlled as to deposit the aluminum at the cathode in a finely divided form and to remove it therefrom and cause it to flow with the electrolyte past the cathode to a chamber where it is removed. In order to insure that the aluminum is deposited in a form that can be readily removed by vibrating the cathode or readily carried by the flowing electrolyte, special addition agents may be provided for the electrolyte. In order to make the electrolyte sufficiently conducting, ingredients such as sodium bromide or potassium bromide form a portion of the electrolyte. In the device illustrated the aluminum particles are filtered from the electrolyte by means of a filter type piston, but other methods for separating the solid and liquid may be used.

Detailed description

In the drawing is a reservoir 10 adapted to contain the electrolyte. A suitable heating means 12 provides sufficient heat to make up for heat lost from the apparatus and to maintain the electrolyte in the chamber at the required temperature necessary to keep the electrolyte in a liquid state when the apparatus is not being operated. Make-up electrolyte may be added to the reservoir from time to time by means of opening 14 and cover 16. Electrolyte is pumped from the reservoir by any suitable pump, which in the form shown is constructed as follows. Extending into the electrolyte in the reservoir is a glass cylinder 18, the lower end of which is in flow communication with the electrolyte by means of openings 20. In the cylinder adjacent the openings is an impeller 22 formed of tantalum. The impeller is secured to a glass rod 24 which is adapted to be rapidly rotated by the electric motor 26. Rotation of the impeller during operation thus causes a flow of the electrolyte continuously through cylinder 18 to an outlet 28, thence to the electrolytic cell proper, indicated generally by the reference numeral 30.

The electrolyte enters the cell and passes through an electrically conducting cup-shaped anode 32 having a series of openings 34 in the lower end thereof. Preferably the anode is formed of carbon. Other insoluble conducting anodes may be used. The openings are so arranged as to direct the electrolyte downwardly toward a cathode 36.

In the form shown the cathode is a rod of tantalum curved to form a ring, the ring being joined to a rod 38 mounted for oscillation within a sleeve 40 adjustably secured to one wall 42 of the cell. The sleeve and rod pass through the wall. The rod 38 is adapted to be rapidly vibrated or rocked back and forth within the sleeve by means of rod 44 fixed thereto at one end, connecting rod 46 pivoted at the opposite end of rod 44, eccentric 48 and electric motor 50. The rapid rocking or vibration of the cathode removes the aluminum therefrom in finely divided form. The aluminum tends to deposit in the form of feathery "trees" or dendrites and advantage is taken of this. Certain addition agents may be added to the electrolyte to control more fully the deposition and cause the formation of the aluminum in finely divided form. The source of electric current is connected in any desired manner to the anode and cathode. The positive side of the current source may be connected to a flange 37 of the anode, for example, while the other side of the current source may be connected to arm 44 connected to the cathode.

The aluminum particles flow with the circulating electrolyte from the electrolytic cell through the outlet 56 and through the tube 58 to a filter chamber indicated generally by the reference numeral 60. Within the filter chamber is a piston element 62 of carbon or other suitable material, said element having openings 64 in the head thereof. Above the head of the piston is a filter element 66. In the device illustrated the filter element is a glass fabric. The purpose of the glass filter and the openings in the head of the piston is to separate the aluminum particles from the electrolyte and to cause the particles of aluminum to collect on the filter element. By means of a glass rod 68 connected to the head of the piston, the piston and filtering element with the particles of aluminum thereon are raised above the inlet in the filter chamber to bring the aluminum particles in contact with a second piston 70 within the filter chamber. In the form shown the piston 70 is of carbon. The aluminum particles are pressed together and form a "cake" or mass 71 which adheres to the piston 70, and thus removes the "cake" from the active filter area so as to permit better flow and also to keep the "cake" away from the electrolyte which may contain small amounts of bromine and might thus otherwise dissolve some of the metal. Mechanical means may be used for suspending the cake from piston 70. The "cake" of metal is gradually built up by successive additions and preferably extends above the level of the electrolyte, thus permitting the electrolyte to drain off. The piston 70 may be removed from time to time by means of a tubular glass rod 72 secured thereto, a cover 74 of the filter chamber being removed during the removal of the piston 70, and all or a portion of the "cake" of aluminum may be removed from the piston 70.

The strained electrolyte leaves the filter chamber through an outlet 75 and returns to the heated reservoir 10 by means of tube 76. In the form of apparatus illustrated, the pump 22, etc., moves the electrolyte to the cup-shaped anode and the flow of electrolyte from this point to the reservoir 10 is due to the force of gravity acting thereon.

As the aluminum is set free at the vibrating cathode, bromine is liberated at the anode, which is centrally arranged in the upper portion of the cell. The free bromine boils up through the hot electrolyte. It is important to maintain high temperatures so that the bromine will not be too soluble in the electrolyte and temperatures approaching the boiling point of the bromine-free electrolyte are desirable. Under these conditions the aluminum halide from the electrolyte will boil off with the bromine, and to make a partial separation of the two and return the aluminum bromide to the cell, the vapors pass through a reflux column. This comprises a glass tube or receptacle 80 nearly filled with glass rings or beads 82. The top of receptacle 80 is closed by a glass cover 81. Surrounding a portion of receptacle 80 is an air chamber 84 having an air outlet 86 and an air inlet tube 88. Most of the vaporized aluminum bromide leaving the cell is condensed by the condenser-reflux column and flows back into the cell. A small amount of the aluminum bromide and the bromine pass out of the reflux-condenser through an outlet 90 arranged near the top thereof, and by means of a passage 92 enter a glass receiver 94. A water condenser 96 condenses any uncondensed bromine and aluminum bromide vapors and returns the same to the receiver.

The design of the anode is important. The bromine must be evolved rapidly in order to avoid the formation of a gaseous film which increases the electrical resistance of the cell. The anode must be designed to be as close to the cathode as possible in order to keep the cell resistance at a minimum. Some circulation of electrolyte past the anode is necessary in order to avoid the formation of a layer of low conductivity; too much stirring is to be avoided as it promotes the solution of the bromine in the electrolyte with the consequent redissolving of the aluminum. The electrical resistance of the anode should be as low as possible. Several forms of anodes have been used in accordance with the above requirements, the form shown in the drawing being preferred. The bottom of the anode is turned to a radius so that it will fit within the cathode and it has a streamlined surface for the free removal of the bromine.

It is important in the operation of the cell that the surface of the anode not be allowed to become a poor conductor of electricity. Under certain conditions, particularly after moisture has had access to the electrolyte, a high resistance film may be built up on the anode. For this reason, the electrolyte must at all times be protected from the introduction of even small amounts of water, in order to assure continuous satisfactory operation of the cell for long periods of time.

The requirements for the cathode are that it should be a good conductor and so shaped that the flow of electric current will be equally distributed and so that it will not obstruct the flow of liquid or of solid metal particles. High current densities are applied so that the deposited metal will be in a form which can be readily dislodged. The upper limit of electrical current in any particular application is governed by the amount of heat generated and this is dependent upon the electrical resistance of the cell. The amount of heat generated should not be such as to cause too vigorous boiling of the electrolyte. Another factor to be considered in the determination of the maximum current is the energy efficiency desired. The electrical energy lost in the internal resistance of the cell as heat, varies with the square of the current, while the amount of metal produced varies directly as the current. The current used in practice in the cell depends consequently upon the economic balance between pounds of metal produced per hour, and kilowatt hours per pound required to produce it.

In one form and size of apparatus constructed in accordance with the invention from 50 to 225 amperes of current have been passed through the electrolyte in a cell having a diameter of six inches. Current densities as high as approximately 15,000 amperes per square foot of cathode area have been used. Good current efficiencies in the range of 80 to 90% have been consistently obtained.

The composition of the electrolyte may vary considerably. It is at present preferred as a matter of experience and compromise that the sodium bromide (when this is used as the current carrier) be about 24% of the electrolyte, the balance being aluminum bromide. Lower proportions of sodium bromide increase the resistance of the electrolyte, while higher proportions reduce the resistance. Considering the electrical resistance alone, the ideal would be the largest possible amount of sodium bromide. The temperature of the electrolyte preferably should be maintained as near the boiling point of the electrolyte as can be in order to remove the bromine as rapidly as possible from the vicinity of the electrode and to keep the electrolyte as free of bromine as possible. In view of this, the lower the concentration of sodium bromide the lower the permissible operating temperature, while the higher the concentration of sodium bromide the higher the required operating temperature. With the at present preferred bath composition (24% sodium bromide and 76% aluminum bromide) an electrolyte temperature of about 850° F. has been used with success. With an electrolyte composed of 10% sodium bromide and 90% aluminum bromide an operating temperature of about 500° F. may be used, while with an electrolyte composed of 20% sodium bromide and 80% aluminum bromide an operating temperature of 650° F. may be used.

In order to ensure that the electrolyte flow through the cell in as near streamline flow as possible, the anode is so designed as to distribute the electrolyte substantially uniformly over the cross section of the cell. In the form illustrated the aluminum released from the cathode flows downwards with the electrolyte. The rate of flow of the electrolyte should be fast enough so as to continuously remove the aluminum from the cell and still not agitate the bath enough to cause the bromine to redissolve any appreciable amount of the aluminum.

It has been found desirable to add small amounts of certain substances to the bath or electrolyte in order to control the size of the particles of aluminum. Under some conditions of operation, especially with very pure materials, or on prolonged electrolysis of less pure materials, the aluminum forms moss-like aggregations, which, when detached from the cathode, tend to agglomerate in large pieces of the mossy, porous type up to an inch or more in diameter. Such large pieces are undesirable in that they do not flow through the cell properly since they are subjected to diverse liquid currents and to mechanical striking by the vibratory cathode. As a result they may be subjected to the action of bromine in the cell and partially dissolved, thus resulting in a decrease in the current efficiency of the cell. The large pieces also have a tendency to clog the connecting tubes to the filter chamber. We have found that small amounts of such materials as naphthalene, phenanthrene, or anthracene when added to the electrolyte prevents the formation of the large particles of aluminum and thus obviates the above mentioned disadvantages of such large particles. One part of the addition agent in about a quarter of a million parts of electrolyte has proven sufficient. The addition agent must be replenished from time to time as needed. Other addition agents which have been used are lubricating oil, rubber and the like. Although we do not wish to be bound by any definite theory, we believe that the mechanism of the action is about as follows: When the addition agent is added to the hot electrolyte, it decomposes and forms insoluble colloidal carbon which is absorbed on the clean and active surfaces of the aluminum particles so as to keep the particles from sticking or welding together to form large particles. In accordance with our theory organic materials which decompose in aluminum bromide at bath temperatures to form colloidal carbon may be used effectively. We prefer to use hydrocarbons or compounds containing little or no oxygen so as to prevent the formation of aluminum oxide as a final product to contaminate the bath.

Due to the fact that aluminum bromide solutions of bromine are very corrosive to most metals, especially at the high temperatures used herein, it is necessary to use materials that are not attacked thereby. In the form of apparatus shown, the cell proper, the filter chamber, the reservoir and the passages connecting the same are formed of Pyrex glass. It is contemplated that other vitreous and ceramic materials, as well as enamel surfaces may be used, as well as carbon when its electrical properties permit. While it is at present preferred that the anode be of carbon it may be formed of tantalum. The best results have been obtained with a cathode formed of tantalum. It is contemplated that the cathode may also be formed of carbon.

The "cake" of aluminum after removal from the filter chamber is a coherent, spongy mass which may be readily broken up. It contains small amounts of aluminum bromide and sodium bromide (when sodium bromide is used as the current carrier). The "cake" of aluminum may be heated in an electric muffle or other furnace to melt the aluminum. During the heating the small amount of aluminum bromide is distilled off and may be recovered for return to the apparatus. The sodium bromide and the aluminum melt and the latter separates into a lower layer which may be drained off and may be cast into pigs. Remarkably pure aluminum has been produced in accordance with the invention.

We wish it to be understood that we do not desire to be limited to the exact details of construction and operation shown and described, for obvious modifications will occur to a person skilled in the art.

We claim:

1. The process of producing aluminum which comprises, flowing a stream of a fused, non-aqueous electrolyte comprising essentially aluminum bromide and a bromide of the class consisting of sodium bromide and potassium bromide downwardly from an anode to a vibrating cathode, passing an electric current from the anode to the cathode through the flowing stream of electrolyte while the electrolyte is at substantially its boiling point to liberate aluminum at the cathode in solid, particulate form and to liberate bromine at the anode, moving the electrolyte and the aluminum particles therein that become detached from the cathode to a point beyond the cathode, and separating the aluminum particles from the electrolyte, the percentage of aluminum bromide in the electrolyte varying from about 76 to 90.

2. A process as in claim 1 in which the electrolyte has added thereto one part in about a quarter of a million parts of electrolyte, of an addition agent of the class consisting of naphthalene, phenanthrene and anthracene.

3. A process as in claim 1 in which the elec-

trolyte has added thereto one part of lubricating oil in about a quarter of a million parts of electrolyte.

4. A process as in claim 1 in which the electrolyte has added thereto one part of rubber in about a quarter of a million parts of electrolyte.

5. The process of producing aluminum which comprises, flowing a stream of a fused, non-aqueous electrolyte comprising essentially aluminum bromide and sodium bromide downwardly from an anode to a vibrating cathode, passing an electric current from the anode to the cathode through the flowing stream of electrolyte while the electrolyte is at substantially its boiling point to liberate aluminum at the cathode in solid, particulate form and to liberate bromine at the anode, moving the electrolyte and the aluminum particles therein that become detached from the cathode to a point beyond the cathode, and separating the aluminum particles from the electrolyte, the percentage of aluminum bromide in the electrolyte varying from about 76 to 90.

6. A process as in claim 5 in which the electrolyte has added thereto one part in about a quarter of a million parts of electrolyte, of an addition agent of the class consisting of naphthalene, phenanthrene and anthracene.

7. A process as in claim 5 in which the electrolyte has added thereto one part of lubricating oil in about a quarter of a million parts of electrolyte.

8. A process as in claim 5 in which the electrolyte has added thereto one part of rubber in about a quarter of a million parts of electrolyte.

9. The process of producing aluminum which comprises, flowing a stream of a fused, non-aqueous electrolyte comprising essentially aluminum bromide and sodium bromide downwardly from an anode to a vibrating cathode, passing an electric current from the anode to the cathode through the flowing stream of electrolyte while the electrolyte is at substantially its boiling point to liberate aluminum at the cathode in solid, particulate form and to liberate bromine at the anode, moving the electrolyte and the aluminum particles therein that become detached from the cathode to a point beyond the cathode, and separating the aluminum particles from the electrolyte, the percentage of aluminum bromide in the electrolyte being about 76.

WHEELER G. LOVELL.
NELSON E. PHILLIPS.