UNITED STATES PATENT OFFICE.

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ELECTROLYTIC SEPARATION OF METAL.

948,681. Specification of Letters Patent. **Patented Feb. 8, 1910.**

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To all whom it may concern:

Be it known that we, Edwin M. Chance, residing at No. 4429 Chestnut street, in the city of Philadelphia, county of Philadelphia, and State of Pennsylvania, and Eleanor Kent, residing at No. 45 Fairview avenue, Lansdowne, in the county of Delaware and State of Pennsylvania, have jointly invented a new and useful Process for the Electrolytic Separation of Metal, whereof the following is a specification.

Our invention is primarily intended for the "winning" of metals from mattes or speisses, although it is adapted to the separation of metals from various alloys, or other compounds.

The process is based upon our discovery that when a matte, speiss, or other metallic compound, in a fused condition, is made the anode of an electrical circuit, in conjunction with a fused electrolyte of proper character, electrolysis may be so conducted as to select one or more of the metallic components of the anode and deposit it or them at the cathode, which latter may be either a solid, or may be itself in a fused condition. The fused electrolyte must be of such character that its anion has affinity for the metallic component, or components, whose separation from the fused anode is sought, and, under some circumstances, may be one whose anion also has affinity for other of said metallic components than the one or ones whose separation and deposit are desired. In the latter case the electrical conditions must be so controlled as to permit selective action, whereby only that metal, or those metals, whose recovery is desired shall undergo electrolytic deposition to any substantial extent.

In order to more fully explain the rationale of our invention, we will first describe a typical process, in which the anion of the fused electrolyte has substantial affinity for only one of the metallic components of the fused anode. In this instance the compound to be treated may consist of an alloy of lead and silver, and the electrolysis, by means of which the pure lead is recovered at the cathode, may incidentally tend to purify the silver residuum in the anode, though this last mentioned feature is not the direct purpose of the process. An alloy of lead and silver, say containing from 2 to 5 percent. of silver, is maintained in a fused condition in a suitable receptacle, and the fused electrolyte is superimposed upon the surface thereof. This electrolyte is one whose anion has an oxidizing action, such as the double silicate of lead and sodium. An electrode of proper character, such as carbon, iron or other substance inert under the conditions of use, is submerged in the fused metallic compound, so that the entire upper surface of the latter, which is in contact with the electrolyte, becomes the anode. The cathode, (in this instance preferably of carbon or iron) is immersed in the electrolyte in proper isolation from the anode surface and the circuit is then established. Since the anion of the fused electrolyte has, under the conditions mentioned, substantially no affinity for the silver, selective electrolysis of the lead ingredient will occur, and the current density and E. M. F. may be as high as convenience dictates, since the crowding of the current will not interfere with the selective action, which is here due to the practically preponderant affinity of the anion of the electrolyte for one of the metals. The process may be continued until substantially all of the lead has been recovered. Where, however, the anion of the electrolyte has substantial affinity for more than one metallic component of the fused anode, it is necessary, in order to insure selective deposition that the current conditions shall be controlled. As a typical instance of such process, we state the following: The compound to be treated is a copper-iron matte, containing copper 49.8 percent., iron 22.3 percent., sulfur 23.3 percent., the remaining constituents being negligible, and it is desired to "win" the copper by electro-deposition at the cathode. In this instance, the fused electrolyte may consist of an alkaline silicate, such for instance, as sodium and potassium meta-silicate, which may with advantage contain about 2% of manganese sesquioxid, to increase fluidity. While the anion of this electrolyte will form a compound with both the iron and the copper, it is a well-known fact that the heat of formation of the respective compounds is markedly different, that of the iron being substantially higher than that of the copper. Under these circumstances, we have discovered that notwithstanding the affinity of the anion of the electrolyte for each of the metallic components, the electrolysis may be so controlled as to only deposit that metal whose compound with the anion has the lesser heat of formation. This is effected by limiting the E. M. F. to an intensity only sufficient for dissociation and deposition of the desired metal from the electrolyte. We believe this phenomenon to be due to the fact that until a certain difference of potential across the poles of the cell is attained, the decomposition of the now metalliferous electrolyte is wholly preferential as distinguished from being distributed in different ratios between the metallic constituents, and that consequently, until the limit is passed, substantially no decomposition whatever occurs as to that ingredient, the heat of formation of whose compound is markedly greater. Whether this theory be the correct one or not, we have found in practice that the required selective action does take place, for instance, with the copper-iron compound we have just described, under the following conditions: A source of current having an E. M. F. of two volts was employed, the external resistance being 1.8 ohms, the current flowing being .14 amperes, the temperature of the fused anode being from 1000 to 1200 degrees centigrade, the distance between the anode and cathode being 6 millimeters, the area of the fused anode surface being 4 square centimeters, and the cathode being an iron rod of 5 millimeters in diameter, immersed in the electrolyte to a depth of 1 centimeter.

Broadly speaking, the two types of our process are identical in those particulars which are of the essence of the invention, viz.: the employment of a fused anode and a fused electrolyte, and the variation between them may be said to consist in the fact that the first mentioned type depends substantially upon selective avidity of attack upon the anode, while the second depends substantially upon the relative reluctance of decomposition of the components formed by the attack.

Having given the foregoing typical illustrations of our process; we point out the fact that it is not to be restricted to the winning or separation of any one metal or group of metals, and that, furthermore, a great variety of electrolytes are available for use in the process. It is obviously impossible in this specification to designate by name, all the metals and all the electrolytes which lend themselves to our process, but we can comprehensively state the following rules for its conduct, viz.: that both anode and electrolyte shall be in a fused condition, as distinguished from aqueous or other solution; that the anion of the electrolyte shall have substantial affinity for at least that component of the fused anode whose electro-deposition at the cathode is sought; that if the anion of the electrolyte has substantial affinity for more than one of the metallic components of the fused cathode, the process can only be selectively employed for the deposition at the cathode, of the metallic component, or components, the heat of re-action of whose compound, or compounds, with the electrolyte anion, is substantially less than that of other component, or components, whose deposition is not then desired; and that in this latter case, the difference of potential across the cell must be so controlled as not to afford the energy necessary for the decomposition of the anion compound, whose metallic component has the higher heat of formation with the anion, and for the deposition of said metallic component. This latter condition may be ascertained tentatively in any particular instance by an initial test, and the requisite electrical conditions thus determined may be maintained for commercial practice.

Having thus described our invention, we desire to state, that we are, of course, aware of the fact that electrolysis of mattes and speisses has been attempted in the wet way, the matte or speiss in a solid condition being made the anode of the circuit. But apart from other distinctive characteristics of our process as compared with such processes, a fundamental difference of great practical importance lies in the fact that the fused condition of the anode permits the continuous and successive presentation of all portions of the desired metal to the action of the electrolyte, whereas when a solid matte or speiss is used as the anode, the action can only proceed by honey-combing the mass, with the result of great loss of efficiency, owing to the local distribution of the metal to be attacked, and its remoteness from the region of greatest advantage, *i. e.*, the plane of contact between the fused electrolyte and the fused anode itself. A further fundamental difference of great practical importance lies in the fact that in humid electrolysis, many impurities, such as arsenic, antimony, and sulfur, are diffused through the electrolyte and cause contamination of the cathode itself, while in our process such impurities at once disappear by volatilization, owing to the temperature at which the process is conducted.

We are also aware that the electrolysis of fused salts for the production and recovery of one or more of the metallic constituents of such salts has been practiced by others, and that oxids, chlorids, fluorids, and other compounds of metals have been dissolved in fused baths to produce electrolytes from which one or more of the dissolved metals can be recovered by electrolysis; and we are likewise aware that processes to recover metals from fused sulfids, oxids and similar compounds by direct electrolysis have been described by others, but our proc ess above set forth is not intended to include either the robbing of an electrolyte for the production of metal, or the direct electrolysis of fused metalliferous compounds, but on the contrary is limited to electrolytic separation and recovery, selectively effected from a fused anode, by means of a fused electrolyte acting in an intermediate capacity, as a carrier.

We claim,

1. The hereinbefore described improvement in electrolytic separation of metal, which consists in subjecting to the passage of an electric current, a fused metalliferous anode, and a fused electrolyte whose anion has selective affinity for a metallic component or components of the anode; and depositing the selective metallic component or components at the cathode, substantially as set forth.

2. The hereinbefore described improvement in electrolytic separation of metal, which consists in subjecting to the passage of an electric current, a fused metalliferous anode, and a fused electrolyte whose anion has affinity for metallic components of the anode and tends to form therewith compounds having markedly different heats of formation; controlling the difference of potential across the cell to effect selective decomposition of metal; depositing at the cathode the metal, or metals, the heat of formation of whose anion compounds is relatively low; and retaining in the electrolyte the metal, or metals, the heat of formation of whose anion compounds is relatively high, substantially as set forth.

In testimony whereof, we have hereunto signed our names, at Philadelphia, Pennsylvania, this thirteenth day of April 1908.

EDWIN M. CHANCE.
ELEANOR KENT.

Witnesses:
VERNON B. MILLER,
JAMES H. BELL.