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PROCESS AND APPARATUS FOR THE SEPARATION AND RECOVERY OF METALS

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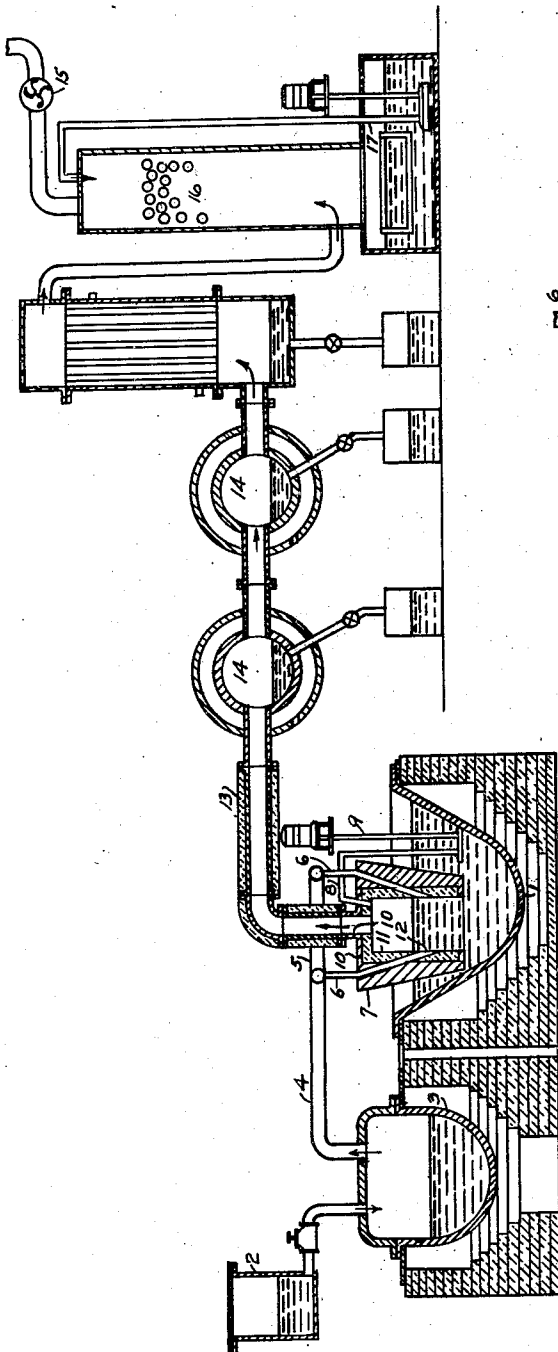


Fig 1

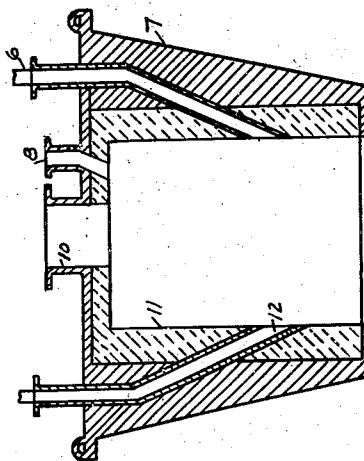


FIG 2

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## UNITED STATES PATENT OFFICE

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## PROCESS AND APPARATUS FOR THE SEPARATION AND RECOVERY OF METALS

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9 Claims. (Cl. 75-63)

This invention relates to a process and apparatus for the separation and recovery of constituents of metals and alloys.

It is known and a subject of numerous patents, that certain constituents of metals and alloys can be removed and eventually recovered by a treatment of the molten metals or alloys with halogens or halids. This treatment essentially consists in forcing a stream of the halogen or halid through the molten metals or alloys or by intimately contacting same with the halogen or halid. Lead, tin, antimony, bismuth, aluminum and zinc in all combinations, can thus be refined or separated from one another.

In the industrial and commercial application of these processes, however, very great and often insurmountable difficulties arise, and in consequence, almost all of the processes remained of theoretical or of laboratory interest only, and did not find useful application in the arts. In a critical study of the processes aiming at the separation of one metal from another by means of a halogen or halid, I have found two very prominent reasons which explain the failure of them in actual practice. The first is the influence of the mass law in heterogeneous systems, and the second is certain very important principles upon which the construction and assembly of practical apparatus rest.

In the processes referred to above, both of these cardinal points were left out of consideration, or only vaguely touched, but never specified. In fact, the true mechanism of these processes were not recognized, their results were misinterpreted or misrepresented and therefore the underlying principles could not be properly established. Simultaneously, the question of practical apparatus, the mode of operation, etc., were left to the imagination or treated with disrespect of chemical and engineering facts and possibilities.

Whenever a molten alloy is treated with a halogen or halid for purposes of separating some of the constituents, a condensed system results. By this is meant that to each composition of the metal phase, there will result a corresponding halid phase and both phases are in equilibrium. The reactions involved in these processes are invariably reversible reactions and are absolutely governed by the ideal mass law. In fact, no better systems can be found for the study of the ideal mass law than one which is composed of two or more metals in one phase and two or more halids in the other phase. It does not matter how widely the molecular percentages of

the respective metals in the alloy phase differ from that in the halid phase, the reaction must stop at an equilibrium and will not proceed until the equilibrium is disturbed. Of course, there are several possibilities for disturbing the equilibrium but from a practical operating view I'll prove that there are only two ways to accomplish this, and that one of these is, in almost all cases, very difficult or even impossible to accomplish.

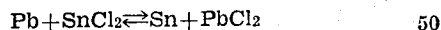
The processes referred to above, to all intents, accomplish the disturbing of the equilibrium by a never ending dilution, that is, each phase of the halid corresponding to a certain phase of the alloy is diluted by a succeeding one, which according to the mass law is of lower concentration of the constituent, the separation of which is the purpose. Translating this in practical terms, many times as much of the reagents will be consumed than an irreversible chemical formula would indicate, resulting in very large quantities of mixed reaction products and consequently, the processes become industrially and commercially unremunerative.

The ideal way of disturbing the equilibrium between the two phases would be the continuous removal from the halid phase of the halid of the constituent, the separation of which is the purpose. In the light of present day knowledge and technical development, this is well high impossible to accomplish or only at such high costs which will make the process above prohibitive.

In between the two extremes of endless dilution and continuous removal of the desirable constituent, lies the possibility of continuous removal of the entire halid phase, thus preventing the dilution of a certain halid composition by the succeeding and necessarily of lower concentration. The separation of the halids can be accomplished then with comparative ease outside the reaction zone, the reactive halid subsequently returned to the reaction zone, making the process industrially and commercially a feasible one.

To illustrate the above, I refer to the well known system of tin+lead+tin chloride+lead chloride.

The reaction in this system can be represented by



According to this, lead can be separated from tin with bichloride of tin or vice versa, tin from lead with chloride of lead. As it is shown, it is a reversible reaction, and in consequence from a given mixture of tin and lead with the molec-

ular quantity of bichloride of tin for instance, less than the molecular quantity of lead will be removed. How much will be removed depends on the ratio of tin to lead in the metal phase. The lower the lead in the metal, the lower will be the chloride of lead in the halid phase.

The system, therefore, will consist of tin and lead in the metal phase and tin and lead chlorides in the halid phase and the phases are in equilibrium. If the lead chloride could continuously be removed from the halid phase, then the stoichiometrical quantity of bichloride of tin would suffice to remove all of the lead.

The melting point of  $\text{SnCl}_2$  is  $215.5^\circ \text{C}$ . and its boiling point is  $620^\circ \text{C}$ .  $\text{PbCl}_2$  on the other hand, melts at  $498^\circ \text{C}$ . and boils around  $950^\circ \text{C}$ . They form eutectic mixtures throughout the range, so that in the reaction zone and at a temperature where both phases are liquid, one cannot be separated from the other.

In the processes referred to above, irrespective of whether a halogen or a halid is used, such a mixed halid phase will result, and inasmuch as one halid is not removed, more and more of the reagent has to be added in order to permit the reaction to proceed in the desired direction.

Regarding the apparatus in which these processes industrially and commercially are carried out, the following has to be taken into consideration:

The quantities of metals and alloys to be treated in modern plants are large. A single batch often amounts to 100 tons or more, requiring, therefore, large quantities of halogens or halids, and yielding large quantities of reaction products.

The processes are carried out with molten metals, therefore at elevated temperature. In fact, the temperature often exceeds  $600^\circ \text{C}$ ., and no metal or alloy is known at the present time, which is capable of resisting the corrosive action of halogens and metallic halids at such a temperature. Nonmetallic materials of construction, on the other hand, some of which resist such an action, are too fragile to entrust them in large scale operations, because an accidental break of them or a break through a temperature shock might endanger the health or even the life of the operators. Gases like chlorine or vapors of the different halids must be forced through the metals in streams of comparatively small diameter, because otherwise through lack of contact, the greater part of the reagent escapes unconsumed. To employ for this purpose materials like glass, fused silica, carbon, graphite, clay or porcelain tubes which the processes referred to profess to employ, would be out of question in large scale industrial operations.

The reaction products, which may be gases, vapors or molten halids, will have to be condensed, collected and handled. They are strong irritants, often very poisonous, always corrosive and also hygroscopic. Again the processes referred to simply collect or condense or otherwise dispose of these products without ever specifying the mode and the equipment, but in an actual operation, these loom up very large problems. In fact, so large, that without solving them, the basic idea itself becomes valueless.

The present invention is a great improvement upon the existing art, is based upon all of the foregoing considerations and will enable those versed in the arts to separate and recover in industrial and commercial operations constituents

of alloys of tin, lead, antimony, bismuth, aluminum and zinc in any combination.

In describing the process and apparatus, reference is made to the accompanying drawing.

In my process, the metal comprising tin, lead, antimony, bismuth, aluminum, and zinc in any combination, is melted in a melting vessel. In industrial operations, the melting vessels are, as a rule, iron kettles set in refractory furnace settings and heated in such a manner that the temperature of the molten metal is closely controlled. The halogen or halid employed in the reaction is contained in commercial containers, such as tank cars or tanks, if they are liquids, or in some other suitable containers if they are solids. From this container 2, the reagent is conducted by some suitable means, such as pressure or conveyor, to a vaporizer. The vaporizer 3 may consist of a heated coil, a boiler or a retort, as the nature of the reagent requires. The vaporized halogen or halid is conducted from the vaporizer by means of a suitable duct 4 to a manifold 5 and distributing pipes 6. These may, if necessary, be insulated to maintain the vapor phase. The distributing pipes connect the halogenator 7. The halogenator is the reaction chamber and consists of a substantial metallic vessel, preferably cylindrical in shape, open at the bottom and with the exception of certain openings closed at the top. One opening 8 is for the admittance of metal circulated by pump 9. Another opening 10 is for the exit of the reaction products. The halogenator is provided with a substantial refractory lining 11 preferably of such nature, that is, capable of withstanding the destructive action of the reagents and reaction products at elevated temperatures. Refractories of high zirconia content are especially suitable. The refractory lining is provided with tuyere openings 12 into which the distributing pipes are inserted.

The halogenator assembly is suspended in the melting vessel in such a manner that the tuyere openings are at all times submerged in the metal at a sufficient depth to cause the reagent passing through them to be as completely consumed as possible.

The reaction products are conducted through duct 13 to a condensing system 14 each member of which is maintained at such a temperature as to condense one constituent of the reaction products only and forward the other or others to the succeeding member or members. Thus one or more members may be maintained at elevated temperatures, and one or more members are maintained at or below atmospheric temperature. Any reagent or reaction product not condensable by ordinary means is exhausted with fan or pump 15 through an absorption tower 16 in which suitable absorbent is circulated by pump 17. In this manner the entire system from the inside of the halogenator on is placed under any desired degree of diminished pressure.

Before I describe the operation of my process in the above apparatus, I will point out how the problems referred to in the preamble are met.

1. The delivery of the halogen or halid to the reaction zone is accomplished in metallic conductors.

2. The introduction of the halogen or halid into the molten metal is accomplished without submerged pipes or tubes of non-metallic construction.

3. The reaction zone is confined within the halogenator, the molten metal providing an efficient seal and thus it is possible to circulate a

large body of molten metal through a relatively small reaction chamber.

4. By obtaining an efficient seal, it is possible to place the reaction zone under any desired degree of vacuum.

5. A reacting chamber is obtained in which mechanical strength, resistance to corrosion and thermal shock is combined.

6. By placing the reaction zone under any desired degree of vacuum, the removal of the entire halid phase is made possible by volatilization at much lower temperature than at or above atmospheric pressure.

7. By placing the condenser system under any desired degree of vacuum at any desired temperature a complete separation of the reaction products is obtained.

8. By the general arrangement of the process and apparatus, in a single assembly, various separations can be accomplished.

To illustrate the process and the function of the apparatus, I'll take the system of tin and lead. It is obvious that whichever of the two constituents is the smaller, that is the one we desire to separate. A small quantity of lead will render the tin unsuited for many uses and vice versa. Thus if we desire to remove lead from tin, we can use either a halogen, such as chlorine, or a halid such as bichloride of tin or tetrachloride of tin. The products of reaction in any case will be a mixture of bichloride of tin and lead chloride. If we use bichloride of tin to remove lead from tin, the procedure is as follows:

The metal, which in this instance is tin containing lead, is melted in the melting vessel. The bichloride of tin is fed from its container, where it is maintained in molten condition, into the vaporizer, which in this instance is a cast iron retort and heated to 650° C. The vapors are conducted through the duct into manifold and distributing pipes which are guarded against loss of heat and are delivered through the tuyères into the metal. The metal circulating pump is started as well as the exhaust pump. The temperature of the metal is held at 712° C. at which temperature and 550 mm. vacuum the entire halid phase vaporizes and passes to #1 condenser maintained at about 540° C. in which only the lead chloride condenses, the bichloride of tin passing to #2 condenser maintained at less than 540° C. and condensed. Both chlorides are in molten condition and are continuously removed from the condensers. The bichloride of tin, of course, is returned to the process. Any product which did not condense is absorbed in absorption tower in which caustic alkali solution is circulated.

The chlorides of tin, lead, antimony, bismuth, aluminum and zinc are all volatile and in vacuo at relatively low temperature. There is also considerable difference in their boiling points to permit rather sharp separations, especially under diminished pressure.

It is also obvious that in a process and apparatus substantially as described many combinations are possible, such as the simultaneous use of a halogen and one or more halid, permitting the simultaneous separation of more than one constituent, which makes the process so much more economical.

In view of the foregoing, what I claim is:

1. Apparatus for the separation and recovery of metallic constituents of metals or alloys of the nature of lead, tin, antimony, bismuth, aluminum and zinc by a treatment of the molten

metal or alloy with halogens or metal-halids or a combination of them comprising a suitable vaporizer for the halogen or halid, means of conducting and distributing the vapors under the surface of the metal in a reaction chamber of metallic outer shell and suitable refractory inner shell, means of suspending the reaction chamber in the main body of molten metal or alloy, means of circulating the main body of molten metal through the reaction chamber, means for maintaining a pressure lower than atmospheric within said reaction chamber, and means for conducting, condensing, and collecting the reaction products resulting from said treatment in suitable conductors, condensers and collecting receptacles, means for maintaining higher or lower than atmospheric temperatures in said condensers and collecting receptacles and means for maintaining a pressure lower than atmospheric within said ducts, condensers and collectors.

2. Apparatus for the separation and recovery of metallic constituents of metals or alloys of the nature of lead, tin, antimony, bismuth, aluminum and zinc by a treatment of the molten metal or alloy with halogens or metal-halids or a combination of them, comprising a suitable vaporizer for the halogen or halid, means of conducting and distributing the vapors under the surface of the metal in a reaction chamber of metallic outer shell and suitable refractory inner shell, means of suspending the reaction chamber in the main body of molten metal or alloy, means of circulating the main body of molten metal through the reaction chamber, means for maintaining a pressure lower than atmospheric within said reaction chamber, means for conducting, condensing, and collecting the reaction products resulting from said treatment in suitable conductors, condensers and collection receptacles, means for maintaining higher or lower than atmospheric temperature in said condensers and collecting receptacles and means for maintaining a pressure lower than atmospheric within said ducts, condensers and collectors, and means for absorbing all uncondensed reagents and reaction products in suitable absorbents.

3. Apparatus for the separation and recovery of metallic constituents of metals or alloys of the nature of lead, tin, antimony, bismuth, aluminum and zinc by a treatment of the molten metal or alloy with halogens or metal-halids, or a combination of them, comprising, a suitable vaporizer for the halogen or halid, means of conducting and distributing the vapors under the surface of the metal at a localized reaction zone within a localizing reaction chamber of metallic outer shell and suitable refractory inner shell, means of suspending the localizing reaction chamber in the main body of molten metal or alloy and means of circulating the main body of molten metal through the localizing reaction chamber.

4. Apparatus for the separation and recovery of metallic constituents of metals or alloys of the nature of lead, tin, antimony, bismuth, aluminum and zinc by a treatment of the molten metal or alloy with halogens or metal-halids, or a combination of them, comprising, a suitable vaporizer for the halogen or halid, means of conducting and distributing the vapors under the surface of the metal at a localized reaction zone within a localizing reaction chamber of metallic outer shell and suitable refractory inner shell, means of suspending the localizing reaction chamber in the main body of molten metal or al-

loy and means of circulating the main body of molten metal through the localizing reaction chamber, and means for maintaining a pressure lower than atmospheric within the said localizing reaction chamber.

5 5. Process for the separation and recovery of metallic constituents of metals and alloys of the nature of lead, tin, antimony, bismuth, aluminum and zinc, which comprises circulating said  
10 metals or alloys in the molten state through a reaction zone whereat the molten metals or alloys are subjected to the action of the vapors of halogens or metal halids, or a combination of them, at a temperature at which the reaction  
15 products are volatilized at a pressure lower than atmospheric and collecting them.

6. Process for the separation and recovery of metallic constituents of metals and alloys of the nature of lead, tin, antimony, bismuth, aluminum and zinc, which comprises circulating said  
20 metals or alloys in the molten state through a reaction zone whereat the molten metals or alloys are subjected to the action of the vapors of halogens or metal halids, or a combination of them, at a temperature at which the reaction  
25 products are volatilized at a pressure lower than atmospheric and condensing said reaction products in interconnected condensers at a pressure lower than atmospheric and at temperatures  
30 which cause the condensing of one constituent in one member of said condensers and absorbing any uncondensed reagent and reaction product in a suitable absorbent.

7. Process for the separation and recovery of  
35 metallic constituents of metals and alloys of the nature of lead, tin, antimony, bismuth, aluminum and zinc, which comprises circulating said metals or alloys in the molten state through a reaction zone whereat the molten metals or  
40 alloys are subjected to the action of the vapors of halogens or metal halids, or a combination of them, at a temperature at which the reaction products are volatilized at a pressure lower than

atmospheric and condensing said reaction products in interconnected condensers at a pressure lower than atmospheric and at temperatures which cause the condensing of one constituent in one member of said condensers, and thus separating one reaction product from another.

8. Process for the separation and recovery of metallic constituents of metals and alloys of the nature of lead, tin, antimony, bismuth, aluminum and zinc, which comprises circulating said  
10 metals or alloys in the molten state through a reaction zone within a localizing reaction chamber suspended in the molten metal or alloy whereat the said molten metals or alloys are subjected to the action of the halogen, a suitable metal halid, or a combination of them, in a  
15 manner that only one constituent is halidized and removing the halid phase from the localizing reaction chamber as fast as it forms, and maintaining a pressure lower than atmospheric with-  
20 in the said localizing reaction chamber and at a temperature sufficient to volatilize the entire halid phase.

9. Process for the separation and recovery of metallic constituents of metals and alloys of the  
25 nature of lead, tin, antimony, bismuth, aluminum and zinc, which comprises circulating said metals or alloys in the molten state through a reaction zone within a localizing reaction chamber suspended in the molten metal or alloy and  
30 injecting into said circulating molten metals or alloys vapors of a halogen, a suitable gaseous or liquid metal halid, or combination of the two, at a predetermined depth and temperature, causing the halidization of one constituent of the metal  
35 or alloy and removing the entire halid phase from the said localizing reaction chamber as fast as it forms by maintaining a pressure lower than atmospheric within the said localizing reaction chamber and at a temperature sufficient  
40 to volatilize the entire halid phase.

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