

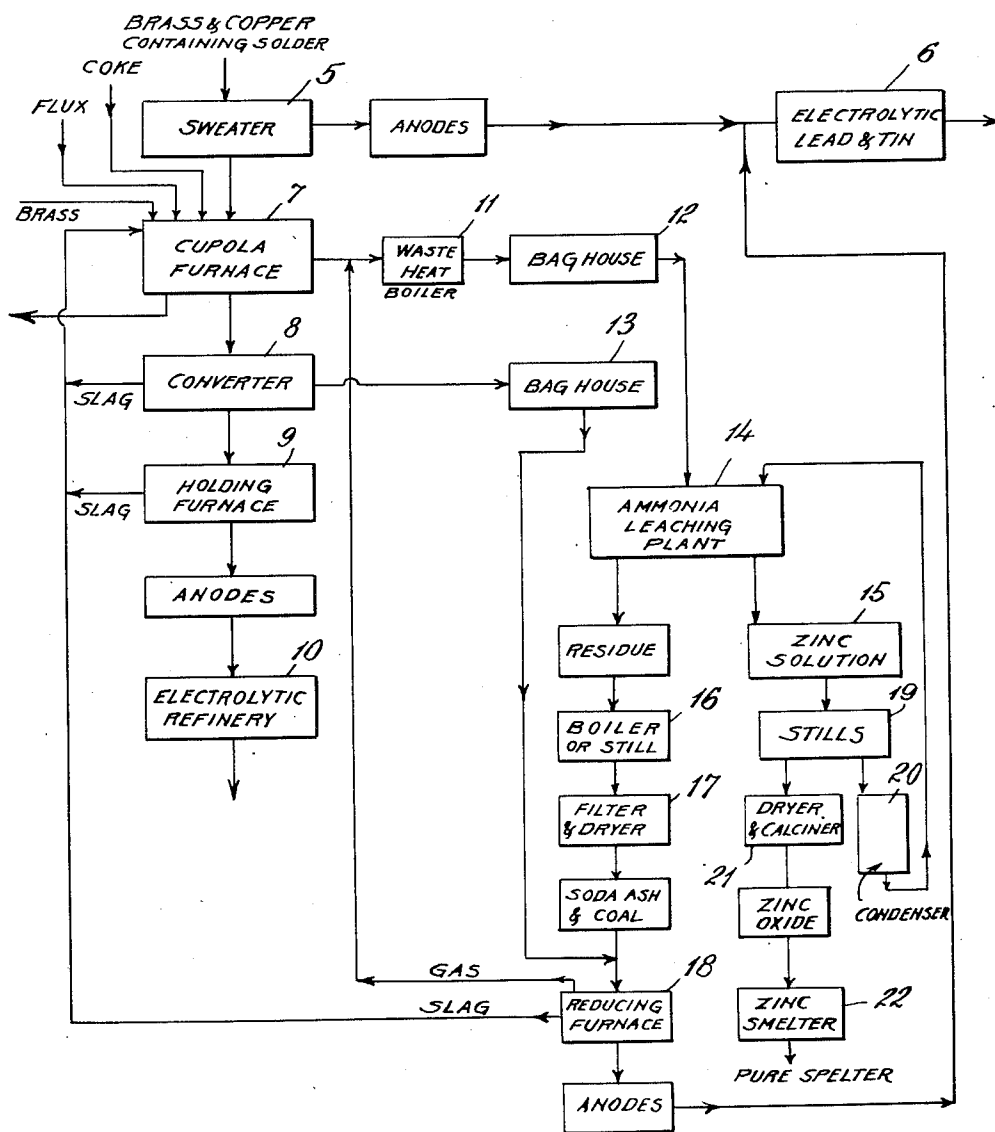
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RECOVERY OF METALLIC ELEMENTS AND ALLOYS

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RECOVERY OF METALLIC ELEMENTS AND ALLOYS

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This invention relates to the recovery of metallic elements and alloys from complex mixtures of metals, and particularly from alloys containing among other elements copper, zinc, tin, lead and iron.

Vast quantities of waste alloy materials consisting of various copper alloys, such as brass and bronze, are available. These alloys contain some or all of the elements mentioned together with nickel, antimony, arsenic, bismuth, silver, gold and sulphur, the compositions varying widely depending upon the use for which the alloys were prepared originally. It is not practicable to classify such materials by composition and consequently it has not been possible heretofore to recover the valuable elements. A large part of the available supply of waste alloy materials has been utilized, therefore, only for the preparation of low grade castings and similar cheap products.

It is the object of the present invention to provide a method of recovering the several elements in substantially pure condition or in the form of valuable alloys, and particularly to afford a method of recovering copper, zinc and tin-lead alloys from complex mixtures or alloys containing these elements.

In carrying out the invention the waste alloy materials are collected from various sources and are mingled indiscriminately without attempt at classification. Such a mixture of alloys contains a proportion of elements, such as tin and lead, which melt at relatively low temperatures. The mixture is initially treated, therefore, to liquefy these more fusible metals. This is accomplished readily by heating the mixture to a relatively low temperature at which the tin-lead alloy is fusible. The fused metal can be separated then from the less fusible residue containing, for example, copper, zinc, iron, nickel, arsenic, antimony and sulphur, together with a proportion of the lead and tin which is not completely separated by liquation. The tin-lead alloy thus recovered can be cast in the form of anodes and subjected to the electrolytic refining method described in the application of Edward F. Kern, Serial No. 222,209.

The residue is then subjected to a smelting operation with carbonaceous material and suitable fluxes to separate the major portion of the iron in a slag and to recover some of the zinc, tin and lead in the form of a fume which is volatilized during the smelting. The molten metal produced by the smelting operation is then blown in a suitable converter to oxidize and remove an additional quantity of iron as slag. Substantially all of the remaining zinc, tin and lead is separated in this operation as fume. The metal residue is blister copper. The latter can then be delivered to a holding furnace wherein it can be subjected to further slagging operations and to "poling," if desired, to purify the copper which can then be cast into anodes and refined by the usual electrolytic refining operation. The pure copper which is deposited on the cathodes can be melted and cast into wire bars, cakes, ingots, etc. adapted for the ordinary purposes for which copper in these forms is utilized in the industry.

The fume is separated from the gases resulting from the smelting operation. It includes zinc, lead, tin and copper, and is subjected to a leaching operation with a carbonated ammoniacal liquor which dissolves the zinc and copper, leaving a residue consisting principally of tin and lead. The residue, after boiling to remove the ammonia, is dried, mixed with the fume recovered from the converter, and treated in a reducing furnace with a mixture of soda ash, lime or other suitable flux and coal to produce a metal consisting of a tin-lead alloy containing small proportions of copper and other elements. This alloy can be cast into anodes and subjected to electrolytic refining treatment in accordance with the method of the above-identified application. The gases from the reducing furnace may be mixed with those from the smelting furnace. The volatilized metals are thus recovered as fume which is leached with a carbonated ammoniacal liquor as hereinbefore described.

The zinc solution recovered by leaching the fume is first treated with metallic zinc to separate copper and is then boiled in a suitable still to separate the ammonia and part

of the carbon dioxide which is condensed and utilized for the preparation of the carbonated ammoniacal liquor employed for leaching. The residue is dried and calcined to produce zinc oxide which may be smelted with a suitable reducing agent such as carbon or dissolved in acid and electrolyzed to produce pure spelter.

As the result of the operation as described the copper and zinc in the alloy material are recovered in a substantially pure form and the lead and tin are separated as a tin-lead alloy which, when purified by electrolytic treatment, is substantially free from arsenic, antimony, sulphur, copper, gold and silver, and adapted, therefore, for numerous commercial uses to which tin-lead alloys are applied.

The invention will be described more particularly with reference to the accompanying drawing which diagrammatically indicates the several steps in the procedure.

Referring to the drawing, 1 indicates a furnace or "sweater" in which the mixed alloy material is heated preliminarily to a temperature at which the tin-lead alloy is fusible and from which the alloy thus separated can be withdrawn, leaving the balance of the material containing copper, iron, etc. The tin-lead alloy is cast into anodes and subjected to electrolysis in the cells indicated at 6 which are operated in accordance with the method described in the application aforesaid.

The residue from the "sweater" is delivered to a cupola furnace 7 together with suitable proportions of coke or other carbonaceous material and a flux, such as lime, and if desired with an additional quantity of brass which is free from tin-lead alloys. The cupola furnace is operated in the ordinary manner to separate a portion of the iron in the form of a slag which is withdrawn through the slag notch and discarded. Zinc, tin, lead and a small amount of copper are separated as fume. The partially purified metal is delivered then to a converter 8 where it is blown with air to oxidize impurities. Iron is separated in the slag and the volatilizable elements escape as fume. The product of this operation is blister copper which is then subjected in a holding furnace 9 to suitable further treatment, including "poling" if desired, to refine the copper. The iron present in the copper, together with other elements such as arsenic and antimony, are removed in the slag from the converter and holding furnace and this slag is returned to the cupola furnace for further treatment with the alloy material therein. The copper, now substantially free from other elements except such slight proportions as cannot be separated by smelting, etc., is cast into anodes and is subjected in the cells 10 to electrolytic refining in accordance with the usual practice. The

cathodes, consisting of the substantially pure copper, are then melted and cast into commercial forms.

The hot gases from the cupola furnace are preferably passed through a waste heat boiler 11 where a considerable portion of the heat is recovered in producing steam for use in the plant. The gases thus cooled are delivered to a bag house 12 wherein the fume is separated. This fume may consist, for example, of zinc, 45%-65%; tin, .75%-15%; lead, 10%-12%; copper, .3%; chlorine .4%. Similarly the gases from the converter 8 are delivered to a bag house 13 where a fume is recovered which may consist of zinc, 40%; lead, 25%; tin, 14%; copper, 1%. It is to be understood that the proportions of the elements in the fume as mentioned are merely illustrative and that these proportions will vary considerably, depending upon the particular character and composition of the materials which are treated.

The recovered cupola fume consisting, as indicated, largely of zinc, is leached in a tank 14 with a carbonated ammoniacal liquor. The liquor may contain ammonia and carbon dioxide in the proportion of one part of each by weight for each part of zinc to be dissolved. The liquor dissolves the zinc and copper forming a zinc solution which is delivered to a tank 15. The residue containing the lead, tin, and some copper, is treated in a boiler 16 to separate the ammonia therefrom. The mixture is then removed in a drier 17. The dried residue is mixed with fume recovered from the converter gases in the bag house 13 and with suitable proportions of soda ash, lime or other fluxes if necessary, and coal and the mixture is treated in a reducing furnace 18 from which a metal consisting of a tin-lead alloy is recovered. The tin-lead alloy can be cast into anodes and electrolyzed in the cells 6. The slag from the reducing furnace 18 contains some valuable elements and it is returned, therefore, to the cupola furnace 7 for further treatment therein. The hot gas from the reducing furnace may be delivered to the waste heat boiler 11 and thence to the bag house 12 for the purpose of recovering the heat and separating any valuable elements present as fume therein.

The zinc solution in the tank 15 is treated with metallic zinc in the form of slabs or powder to separate copper, if present, and the solution is then heated in stills 19 to separate ammonia and part of the carbon dioxide which is condensed in a condenser 20 and returned as carbonated ammoniacal liquor for further use in leaching the fume. Any deficiency of carbon dioxide is replaced by treating the condensate with flue gases containing carbon dioxide. The residue is dried and calcined in a furnace 21 to produce zinc oxide, and recovery of carbon dioxide.

The latter is then subjected to reduction in a furnace 22 to produce pure spelter, or if very pure zinc is desired the oxide may be dissolved in acid, the zinc being then recovered by electrolysis in the usual manner.

5 The method of the Kern application above identified, which is utilized for the purification of the tin-lead alloy, consists briefly in subjecting the tin-lead anodes to electrolysis
10 in an electrolyte containing, for example, lead and tin fluosilicates and free fluosilicic acid, lead and tin fluoroborates and free fluoroboric acid, lead and tin cresol-sulfonate and free cresol-sulfonic acid, or mixtures of such
15 solutions. Preferably these solutions contain also an organic reagent such as gelatin or glue or mixtures of either gelatin or glue with cresol. The amount of the organic addition reagent required is about one part by
20 weight to 3000 parts by weight of the electrolyte. The organic addition reagent should be added periodically to the electrolyte as indicated by the characteristic formation of the cathode deposit. The electrolysis is conducted preferably at a voltage of .3 to .4
25 volts and with a current density of from 12 to 36 amperes per square foot. The temperature of the electrolyte should not exceed approximately 50° C.

30 The electrolysis as described produces substantially pure tin-lead alloys at the cathode, leaving anode residues containing antimony, arsenic, bismuth, copper, silver and gold, if these elements are present in the anodes. The
35 residues may be treated in any suitable manner for the separation of the constituent elements.

The method of refining the tin-lead alloys forms no part of the present invention which
40 relates more particularly to the separation of such tin-lead alloys in impure form from crude alloy materials and the recovery from such materials of substantially pure copper and pure zinc.

45 It is to be understood that the details of the method, including proportions of fluxes and carbonaceous reducing agents, may be varied depending upon the composition of the raw material used, and that various
50 changes may be made, therefore, without departing from the invention or sacrificing any of the advantages thereof.

I claim:—

55 1. The method of recovering copper and zinc from waste alloy material containing these elements, which comprises smelting the alloy material, separating a fume containing the zinc from the gases evolved by the smelting operation, leaching the fume with a solvent for the zinc and recovering the zinc from the solution.

60 2. The method of recovering copper, zinc and a tin-lead alloy from waste alloy materials containing these elements, which comprises smelting the alloy material, separating

a fume containing the zinc, lead and tin from the gases evolved by the smelting operation, leaching the fume with a solvent for the zinc, recovering the zinc from the solution and reducing the residue containing tin and lead.

3. The method of recovering copper and zinc from waste alloy material including these elements, which comprises smelting the alloy material, blowing the metal with air to oxidize and separate impurities in the copper, separating a fume containing the zinc from the gases evolved by the smelting operation, leaching the fume with a solvent for the zinc and recovering the zinc from the solution.

4. The method of recovering copper, zinc and a tin-lead alloy from waste alloy materials containing these elements, which comprises smelting the alloy material, blowing the metal with air to oxidize and separate impurities in the copper, separating a fume containing the zinc, lead and tin from the gases evolved by the smelting operation, leaching the fume with a solvent for the zinc, recovering the zinc from the solution, mixing the residue containing tin and lead with fume separated from gases produced by the blowing operation and reducing the mixture.

5. The method of recovering copper, zinc and a tin-lead alloy from waste alloy materials containing these elements, which comprises smelting the alloy material, blowing the metal with air to oxidize and separate impurities in the copper, separating a fume containing the zinc, lead and tin from the gases evolved by the smelting operation, leaching the fume with a solvent for the zinc, recovering the zinc from the solution, mixing the residue containing tin and lead with fume separated from gases produced by the blowing operation, reducing the mixture and mingling the gases from the reduction with those evolved by smelting before the fume is separated therefrom.

6. The method of recovering copper and zinc from waste alloy material containing these elements, which comprises smelting the alloy material, separating a fume containing the zinc from the gases evolved by the smelting operation, leaching the fume with a carbonated ammoniacal liquor to dissolve the zinc and recovering the zinc from the solution.

7. The method of recovering copper and zinc and a tin-lead alloy from waste alloy material containing these elements, which comprises smelting the alloy materials, separating a fume containing zinc, lead and tin from the gases evolved by the smelting operation, leaching the fume with a carbonated ammoniacal liquor to dissolve the zinc, recovering the zinc from the solution and reducing the residue.

8. The method of recovering copper and

- zinc from waste alloy materials containing these elements, which comprises smelting the alloy material, blowing the metal with air to oxidize and separate impurities in the copper, separating a fume containing the zinc from the gases evolved by the smelting operation, leaching the fume with a carbonated ammoniacal liquor to dissolve the zinc and recovering the zinc from the solution.
9. The method of recovering copper and zinc and a tin-lead alloy from waste alloy material containing these element, which comprises smelting the alloy material, blowing the metal with air to oxidize and separate impurities in the copper, separating a fume containing the zinc, lead and tin from the gases evolved by the smelting operation, leaching the fume with a carbonated ammoniacal liquor to dissolve the zinc, recovering the zinc from the solution, mixing the residue containing tin and lead with fume separated from gases produced by the blowing operation and reducing the mixture.
10. The method of recovering copper and zinc and a tin-lead alloy from waste alloy material containing these elements, which comprises smelting the alloy material, blowing the metal with air to oxidize and separate impurities in the copper, separating a fume containing the zinc, lead and tin from the gases evolved by the smelting operation, leaching the fume with a carbonated ammoniacal liquor to dissolve the zinc, recovering the zinc from the solution, mixing the residue containing tin and lead with fume separated from gases produced by the blowing operation, reducing the mixture and mingling the gases from the reduction with those evolved by smelting before the fume is separated therefrom.
11. The method of recovering copper and zinc from waste alloy material containing these elements, which comprises smelting the alloy material, separating a fume containing the zinc from the gases evolved by the smelting operation, leaching the fume with a carbonated ammoniacal liquor to dissolve the zinc, boiling the liquor to separate the ammonia and part of the carbon dioxide, returning the ammonia and carbon dioxide for further use as a solvent and recovering the zinc from the solution.
12. The method of recovering copper and zinc and a tin-lead alloy from waste alloy material containing these elements, which comprises smelting the alloy materials, separating a fume containing zinc, lead and tin from the gases evolved by the smelting operation, leaching the fume with a carbonated ammoniacal liquor to dissolve the zinc, boiling the liquor to separate ammonia and part of the carbon dioxide, returning the ammonia and carbon dioxide for further use as a solvent, recovering the zinc from the solution and reducing the residue.
13. The method of recovering copper and zinc from waste alloy materials containing these elements, which comprises smelting the alloy material, blowing the metal with air to oxidize and separate impurities in the copper, separating a fume containing the zinc from the gases evolved by the smelting operation, leaching the fume with a carbonated ammoniacal liquor to dissolve the zinc, boiling the solution to separate the ammonia and part of the carbon dioxide, returning the ammonia and carbon dioxide for further use as a solvent and recovering the zinc from the solution.
14. The method of recovering copper and zinc and a tin-lead alloy from waste alloy material containing these elements, which comprises smelting the alloy material, blowing the metal with air to oxidize and separate impurities in the copper, separating a fume containing the zinc, lead and tin from the gases evolved by the smelting operation, leaching the fume with carbonated ammoniacal liquors to dissolve the zinc, boiling the solution to separate the ammonia and part of the carbon dioxide, returning the ammonia and carbon dioxide for further use as a solvent, recovering the zinc from the solution, mixing the residue containing tin and lead with fume separated from gases produced by the blowing operation and reducing the mixture.
15. The method of recovering copper and zinc and a tin-lead alloy from waste alloy material containing these elements, which comprises smelting the alloy material, blowing the metal with air to oxidize and separate impurities in the copper, separating a fume containing the zinc, lead and tin from the gases evolved by the smelting operation, leaching the fume with carbonated ammoniacal liquors to dissolve the zinc, boiling the solution to separate the ammonia and part of the carbon dioxide, returning the ammonia and carbon dioxide for further use as a solvent, recovering the zinc from the solution, mixing the residue containing tin and lead with fume separated from gases produced by the blowing operation, reducing the mixture and mingling the gases from the reaction with those evolved by smelting before the fume is separated therefrom.
- In testimony whereof we affix our signatures.
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