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# (54) METHOD OF REFINING A LEAD-TIN ALLOY

(57) The method of refining lead-tin alloy involves the known process of scorifying the lead, followed by the known process of de-coppering of the lead with sulphur and in the next stage of the process, sulphur is removed to a level of less than 0.001% by means of sodium hydroxide NaOH added at 390°C to 410°C in an amount of 2 to 3 weight amounts of sulphur still in the bath, resulting in a sulphur content of 0.001 to 0.0001% by weight. The metal is then heated to between 610°C and 700°C and metallic aluminium is added in an amount of 0.2 to 0.5 of the sum of the amounts of antimony and arsenic impurities by weight, with the lead being stirred until the metallic aluminium is dissolved, the lead is then cooled to between 370°C and 500°C and coke breeze is added in an amount of: 0.001 to 0.003 by weight of the total refined lead-tin alloy in order to dry the dross formed on the surface of the bath. The dross formed on the surface containing lead and aluminium compounds with antimony, arsenic, sulphur, copper and nickel is collected. The final step is the removal of the residual aluminium with caustic soda NaOH added at 400°C to 480°C by weight in an amount twice the aluminium content of the metal bath. The result of the process carried out is a lead-tin alloy with a content of total impurities such as antimony, arsenic, sulphur, nickel, copper and aluminium of less than 0.001 per cent by weight.

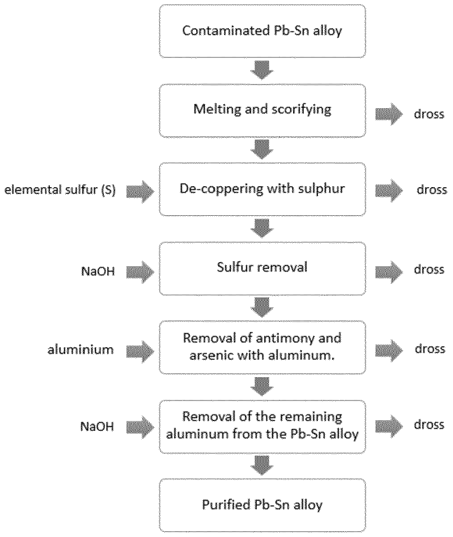


Fig. Technological scheme of the process

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## Description

**[0001]** The object of the invention is a method of refining a lead-tin alloy for use in the nonferrous metal recycling industry, by which a high-purity lead-tin alloy is obtained.

**[0002]** In lead refining, fire processes are predominantly used. The first stage is the so-called scorifying, which is carried out in the same furnaces (boilers) in which the lead was melted. The process involves stirring liquid lead at a temperature of about 450°C, resulting in the formation of so-called scoriae on the surface containing slag inclusions, copper and lead sulphides and intermetallic compounds mainly of copper. Once the lead has cooled to around 350°C, the resulting scales are collected from its surface. The next stage is final de-coppering, where granular elemental sulphur or galena is added to the lead at a ratio of 1 kg sulphur per 1 kg copper at 330 - 340°C. The next stage is refining with the Harris leaching method, which involves adding sodium hydroxide NaOH and sodium nitrate $NaNO_3$ to the lead. The effect of these alkalis is the oxidation of arsenic, tin, antimony and some lead. The oxides formed in the reactions do not dissolve in the lead, allowing them to be easily removed in the form of dross from the surface of the lead bath. Thus, the effect of using refining methods by oxidation is the removal of tin as one of the first elements from the lead bath, which in turn hinders its rational recovery due to large losses to waste.

**[0003]** From the Chinese patent description CN 108728648, a method for producing an alloy with a high content of lead, tin and calcium in the recycling process of lead battery grids is known. The main disadvantage of the process approach described in this patent is that the end result is a lead-tin alloy contaminated with large amounts of calcium and aluminium, which severely limits its further use.

**[0004]** The essence of the invention lies in the use of an aluminium additive for the fire refining of lead-tin alloy. This is a similar process to tin refining. Instead of refining the lead mainly by oxidising the impurities using, for example, the Harris leaching method (which removes the tin), metallic aluminium is added, resulting in intermetallic aluminium compounds with antimony and arsenic that do not dissolve in the lead and tin at the temperature at which the process is carried out. By running the process according to the guidelines, it is possible to achieve a content of the sum of the impurities antimony, arsenic, copper, nickel in the lead-tin alloy of less than 0.001 per cent by weight, without losing the tin contained in the lead.

**[0005]** The method of refining the lead-tin alloy involves the known process of scorifying the lead, followed by the known process of de-coppering the lead with sulphur. The sulphur is then removed to less than 0.001 % by means of sodium hydroxide NaOH added at 390°C to 410°C in an amount of 2 to 3 quantities by weight of the sulphur still in the bath, resulting in a sulphur content of 0.001 to 0.0001% by weight. The metal is then heated to between 610°C and 700°C and metallic aluminium is added in an amount of 0.2 to 0.5 of the sum of the amounts of antimony and arsenic impurities by weight, with the lead being stirred until the metallic aluminium is dissolved, the lead is then cooled to between 370°C and 500°C and coke breeze is added in an amount of: 0.001 to 0.003 by weight of the total refined lead-tin alloy in order to dry the dross formed on the surface of the bath. The dross formed on the surface containing lead and aluminium compounds with antimony, arsenic, sulphur, copper and nickel is collected. The final step is the removal of the residual aluminium with caustic soda NaOH added at 400°C to 480°C by weight in an amount twice the aluminium content of the metal bath. The result of the process carried out is a lead-tin alloy with a content of total impurities such as antimony, arsenic, sulphur, nickel, copper and aluminium of less than 0.001 per cent by weight.

**[0006]** In other words, the way to refine a lead-tin alloy is to use the process of scorifying known for lead. The resulting dross rich in intermetallic compounds of sulphur with copper and arsenic is collected. A further step is also known from the literature for lead refining and tin refining, the process of de-coppering with sulphur, in which granulated sulphur is added to the metal bath at a temperature of about 335°C. The dross formed is pulled off the surface with perforated shovels. The next step is the removal of the sulphur to a level of approximately 0.0001% by weight.

**[0007]** The culminating step in the new lead-tin alloy refining process is heating the metal to 610°C to 700°C and adding metallic aluminium in an amount of 0.2 to 0.5 of the sum of the amounts of antimony and arsenic impurities by weight, with the lead being mixed until the metallic aluminium is completely dissolved. The formation of AlAs and AlSb compounds, which are insoluble in the lead-tin alloy, was confirmed by examination of samples of dross resulting from the refining process. Nickel and copper levels are also reduced during this stage. The lead-tin alloy is then cooled to between 370°C and 400°C and the dross formed on the surface containing lead and aluminium compounds with antimony, arsenic, sulphur, copper and nickel is collected.

**[0008]** The aluminium added to the raw lead is in the form of pure aluminium or aluminium scrap and care must be taken with impurities compacted in the aluminium scrap, as these can transfer to the lead. For example, aluminium must not be contaminated with zinc or magnesium which will transfer to lead when melted. Aluminium is added in portions minimising the possibility of oxidation. Treatments to reduce aluminium oxidation include directly dropping aluminium into the funnel created during lead mixing or by immersing it in a steel lead basket. When aluminium is added, the temperature of the lead is maintained between 610°C and 700°C. The addition of more aluminium than specified does not pose a process problem, but does affect the cost of refining. Once the aluminium has been added and the lead bath

has cooled, coke breeze is added to dry the dross formed on the surface of the lead bath, which is then collected by various known methods, e.g. using a perforated shovel. Dross remains on the shovel, while liquid lead flows through the holes. Once the dross is finally collected, it should be checked whether the expected lead purity has been achieved. If this is not the case, the lead must be reheated to a temperature of 610°C to 700°C and metallic aluminium added to it again in an amount of 0.2 to 0.5 of the sum of the amounts of antimony and arsenic impurities by weight, the lead should be stirred until the metallic aluminium is completely dissolved. The lead is then cooled to between 370°C and 500°C and a drying additive is applied to dry the resulting dross, which in turn facilitates the dross collection from the metal surface using, for example, a perforated shovel.

**[0009]** The final step in the new lead-tin alloy refining process is the removal of any residual aluminium with caustic soda NaOH by weight in an amount equivalent to twice the weight of the aluminium in the metal bath. Adding more caustic soda NaOH will result in loss of tin and adding less will not remove all the aluminium. This process is best carried out at temperatures in the range of 400°C to 480°C.

**[0010]** The result of the above-described process is a lead-tin alloy with a content of total impurities such as antimony, arsenic, sulphur, nickel, copper, aluminium below 0.001%. If there is a need for additional refining operations of lead-tin alloy with elements such as Ag, Bi, Zn, Tl, Te, these are performed by the known methods for fire refining of lead.

**[0011]** The advantage of the method of refining lead according to the invention is primarily that virtually all of the tin is left in the lead. Another advantage is the short time of the entire lead-tin alloy refining process and the reduction of dust emissions containing heavy metals compared to classical lead refining processes.

**[0012]** The method according to the invention is shown in the following embodiments:

Embodiment I. 95 tonnes of metal of composition were melted in a melting furnace (refining boiler): Sb = 6.120%, As = 0.177%, Sn = 1.395%, Ni = 0.0011% and S = 0.003%. Refining of the lead-tin alloy was carried out according to the developed technological scheme. It started with a process of 'lead scorifying', then de-coppering with sulphur and then very thorough removal of sulphur from the lead bath with caustic soda. The lead-tin alloy was then heated to 640°C and metallic aluminium was added in portions for a total of 2,700 kg. Once the lead-tin alloy had cooled to about 420°C, the dross was dried by adding 250 kg of coke breeze and then collected with a perforated shovel. The process resulted in the following lead composition: Sb = 0.001%, As < 0.0001%, Sn = 1.499%, Ni < 0.0001% and S = 0.0001%.

**[0013]** The figure illustrates a process scheme of the new method of refining lead-tin alloy.

**[0014]** Embodiment II. 80 tonnes of metal of composition were melted in a melting furnace (refining boiler): Sb = 5.158%, As = 0.001%, Sn = 6.730%, Ni = 0.0001% and S = 0.002%. Refining of the lead-tin alloy was carried out according to the developed technological scheme. It started with a process of 'lead scorifying', then de-coppering with sulphur and then very thorough removal of sulphur from the lead bath with caustic soda.

**[0015]** The lead-tin alloy was then heated to 680°C and metallic aluminium was added in portions for a total of 1800 kg. Once the lead-tin alloy had cooled to about 450°C, the dross was dried by adding 200 kg of coke breeze and then collected with a perforated shovel. The process resulted in the following lead composition: Sb = 0.005%, As < 0.0001%, Sn = 6.98%, Ni < 0.0001% and S = 0.0001%.

**[0016]** Embodiment III. 80 tonnes of metal of composition were melted in a melting furnace (refining boiler): Sb = 7.740%, As = 0.156%, Sn = 6.020%, Ni = 0.0082% and S = 0.058%. Refining of the lead-tin alloy was carried out according to the developed technological scheme. It started with a process of 'lead scorifying', then de-coppering with sulphur and then very thorough removal of sulphur from the lead bath with caustic soda. The lead-tin alloy was then heated to 680°C and metallic aluminium was added in portions for a total of 1300 kg. Once the lead-tin alloy had cooled to about 450°C, the dross was dried by adding 240 kg of coke breeze and then collected with a perforated shovel. The process resulted in the following lead composition: Sb = 0.001%, As < 0.0001%, Sn = 6.04%, Ni < 0.0001% and S = 0.0001%.

**[0017]** Embodiment IV. 100 tonnes of metal of composition were melted in a melting furnace (refining boiler): Sb = 1.61%, As = 0.075%, Sn = 1.331%, Ni = 0.0011% and S = 0.012%. Refining of the lead-tin alloy was carried out according to the developed technological scheme. It started with a process of 'lead scorifying', then de-coppering with sulphur and then very thorough removal of sulphur from the lead bath with caustic soda. The lead-tin alloy was then heated to 670°C and metallic aluminium was added in portions for a total of 500 kg. Once the lead-tin alloy had cooled to about 420°C, the dross was dried by adding 250 kg of coke breeze and then collected with a perforated shovel. The process resulted in the following lead composition: Sb = 0.001%, As = 0.0004%, Sn = 1.327%, Ni < 0.0001% and S = 0.0001%.

**[0018]** An example of a failed process due to too much sulphur in the lead-tin alloy:

Embodiment V. 90 tonnes of metal of composition were melted in a melting furnace (refining boiler): Sb = 3.8364%, As = 0.387%, Sn = 8.038%, Ni = 0.0486% and S = 0.0486%. Refining of the lead-tin alloy was carried out according to the developed technological scheme. It started with a process of 'lead scorifying', then de-coppering with sulphur, but the sulphur removal was omitted by going straight to heating the lead-tin alloy to 680°C and adding metallic aluminium in portions totalling 1,000 kg. The process resulted in a dusty grey dross on the surface of the lead, with an intense hydrogen sulphide smell, and the following lead composition was obtained:

Sb = 3.8211%, As = 0.354%, Sn = 7.975%, Ni = 0.0456% and S = 0.0127%. As one can see, antimony, arsenic or nickel have stayed at the same levels, only the sulphur content has decreased.

## Claims

1. The method of refining a lead-tin alloy consists of the known process of scorifying the lead followed by the known process of de-coppering of the lead with sulphur, the next stage of the process being **characterised in that** sulphur is removed to a level of less than 0.001 % by means of sodium hydroxide NaOH added at 390°C to 410°C in an amount of 2 to 3 quantities by weight of sulphur still in the bath, resulting in a sulphur content of 0.001 to 0.0001% by weight, the metal is then heated to 610°C to 700°C and metallic aluminium is added in an amount of 0.2 to 0.5 of the sum of the amounts by weight of antimony and arsenic impurities, the lead being stirred until the metallic aluminium is dissolved, the lead is then cooled to 370°C to 500°C and coke breeze is added in an amount of 0.001 to 0.003 by weight of the total refined lead-tin alloy to dry the dross formed on the surface of the bath, and then the dross formed on the surface containing lead and aluminium compounds with antimony, arsenic, sulphur, copper and nickel is collected, the final step is the removal of the residual aluminium with caustic soda NaOH added at 400°C to 480°C in an amount equal to twice the aluminium content of the metal bath, the result of the process is a lead-tin alloy with a content of the sum of the impurities with elements such as antimony, arsenic, sulphur, nickel, copper and aluminium below 0.001% by weight.

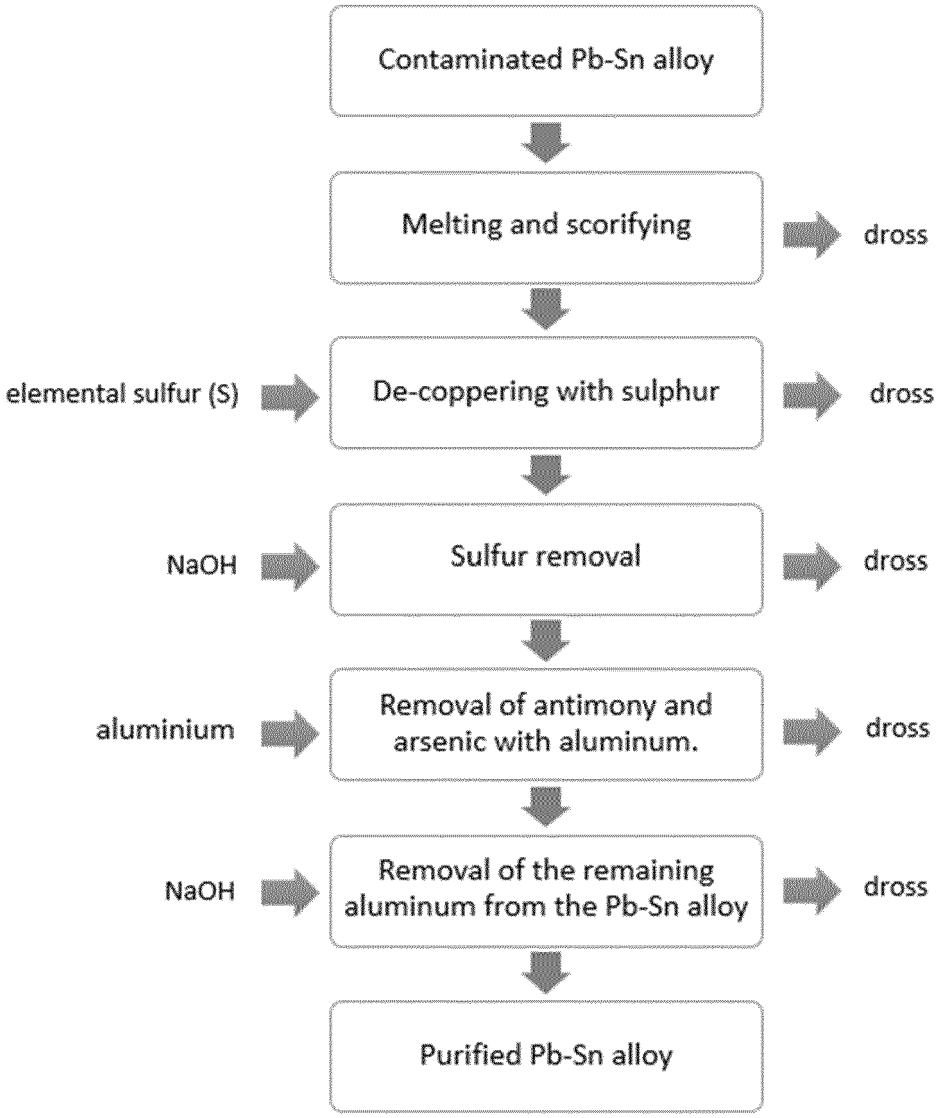


Fig. Technological scheme of the process

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# EUROPEAN SEARCH REPORT

Application Number
EP 23 15 7067

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The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| The Hague | 21 July 2023 | Rosciano, Fabio |

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