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TREATING LEAD ALLOYS

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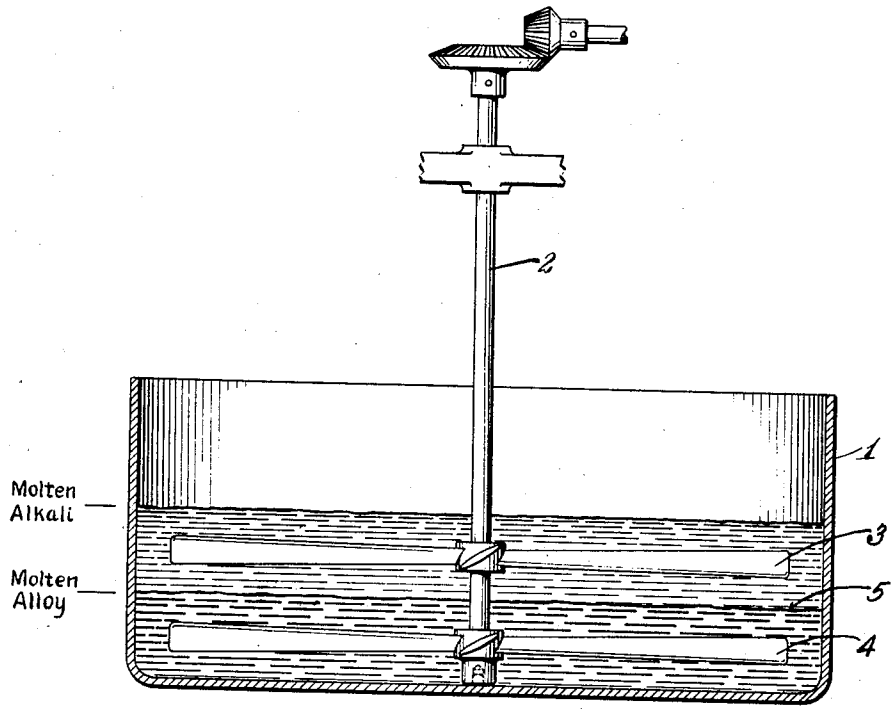

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TREATING LEAD ALLOYS

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This invention relates to a process whereby alloys relatively high in lead are treated for the purification of such alloys and the removal of all or part of the arsenic, tin and antimony contained therein. This process also removes to a greater or less extent other impurites such as iron, zinc and copper. The metal or alloy resulting from this treatment possesses superior advantages on account of its great fluidity when molten and evenness of grain when solid.

The alloys which may be advantageously treated by this process include the following:

First: Antimonial lead which is a by-product obtained in the smelting of lead ores. Such antimonial lead contains excessive quantities of arsenic, which renders the alloy unsuitable for many purposes without purification.

Second: Secondary alloys which are obtained by the smelting of drosses and other materials such as old storage battery plates which have served their use. Secondary alloys also include impure type-metal and similar metals which having been used have become so impure as to render them unsuitable for further use without purification. In many cases these secondary alloys are a drug upon the market. By the process described herein they are rendered more valuable because by this process certain impurities and constituents may be removed more or less selectively.

This process removes arsenic, tin and antimony and recovers them as compounds or as metals derived therefrom having commercial value. The process also removes oxides which may be in colloidal suspension in the alloys which impair their fluidity when liquid and their internal structure when solid. By way of illustration suppose we have an alloy containing

	Per cent
Lead	85
Arsenic	.5
Tin	3.
Antimony	11.5
Other impurities	traces
Total	100.00

I am able by this process to remove arsenic and other impurities with very little removal of tin or antimony and substantially no removal of lead leaving a clean metal suitable for the manufacture of type metals containing substantially only tin, antimony and lead. If the original alloy contained copper, the copper is also removed to the extent that it becomes insoluble in the alloy resulting from the treatment. By this process the treatment can be carried further to remove all or part of the tin according to the product desired. In removing the tin a small portion of the antimony may also be removed. If it is desired the treatment can be carried further so that all or part of the remaining antimony may be removed and if all of the antimony is removed a clean soft lead is obtained. In this latter case a very small amount of the lead may also be removed. The amount of lead so removed may be ultimately recovered and in any case is insignificant as affecting the economy of the process.

Substantially the process consists in bringing the molten alloy into intimate contact with a molten alkali to which from time to time, and according to the purpose in view, an oxidizing agent, preferably sodium nitrate, is added. The amount and character of the alkali used and the amount of the oxidizing agent used are determined by the end desired. The chemical reactions taking place are, first, the oxidation of the metals which are to be removed; and second, the combination of such oxides with the alkali and the compounds so formed becoming dissolved or suspended in the alkali. To perform this operation a cast iron or cast steel kettle is used. The shape of the kettle is of importance only as affecting the economy of the operation. I prefer to use a relatively shallow kettle, that is, a kettle having a diameter of more than twice its depth, or about as shown in the accompanying drawing wherein the kettle may be assumed to be about seven feet in diameter and about three feet high. This is for the purpose of having a large interface at the point of contact of the molten alloy and the molten alkali. The kettle is provided with a stirring apparatus consisting of a vertical

shaft 2 to which are attached stirrer arms 3 and 4. I prefer to have two sets of stirrer arms or their equivalent—one in the mass of metal and the other in the alkali. A third stirrer arm at a higher level for the purpose of breaking down foam may be desirable. The stirrer is operated at as high a speed as is practicable without throwing any of the contents of the kettle over the kettle edge. The high speed is for the purpose of bringing about as rapid a change of surface at the interface 5 as possible with the result that the metal and alkali may react with each other as rapidly as possible. Stationary baffles may be provided on the kettle to promote the change of interface. There is very little commingling of the alkali with the alloy. This is due to the great difference in their specific gravities. The alloy and alkali may be melted in this kettle or placed in it in a molten state. The kettle is heated by any suitable device. I prefer to keep the alloy and alkali at a temperature somewhat above 350° C. When the alloy and alkali have the suitable temperature an oxidizing agent such as sodium nitrate is introduced gradually, the stirrer being in operation. Almost immediately a liberation of gas occurs which gas is nitrogen. In some cases the odor of ammonia is noticed, formed by the action of nascent hydrogen upon the nitrogen liberated. Apparently when ammonia is formed it is due to the action of the alkali upon the alloy with the liberation of hydrogen in the nascent state. The main reaction, however, results in the liberation of nitrogen gas. Apparently the reactions that take place are according to the following equations:

1. $2As+4NaNO_3=As_2O_5+2Na_2O+2N_2$
2. $5Sn+4NaNO_3=5SnO_2+2Na_2O+2N_2$
3. $2Sb+4NaNO_3=Sb_2O_5+2Na_2O+2N_2$

Having used the desired amount of alkali and the desired amount of nitrate, the alkali layer will have become somewhat pasty. The stirring is then preferably continued without further addition of oxidizing agent to complete the reduction of the oxidizing agent. This may require from one-half hour to an hour. The alkali mass is then removed, as by skimming and set aside for further treatment and the residual metal is removed. In this operation the alkali acts principally as a diluent of the oxidizing agent used and as a carrier of the metal compounds produced. The thickening of the alkali is due to the distribution through it of the metallic compounds formed. These metallic compounds may be sodium arsenate, sodium stannate and/or sodium antimonate.

From the foregoing it will be seen that my process differs from previous attempts to purify secondary lead alloys in the respect that I maintain an interface of very large area between the strata of molten alloy and molten alkali and constantly and continuously change the material of the contacting faces of both strata so as to bring about a rapid reaction of the one upon the other, and I have found that in this way the removal of the impurities can be conducted, not only on an inexpensive and commercially profitable basis, but that the extent of separation is subject to close control, so that I can selectively remove some or all of the tin or tin and antimony according to the requirements of the ultimate product and further that the apparatus and power required are thereby reduced to a minimum, no pouring or circulating of the metal through the alkali being required or desirable. Very little labor, power and fuel are needed. The relatively light pasty alkali mass is easily removed. The metal remaining in the kettle may be easily pumped or otherwise transferred to moulds or to other kettles for standardization. Practically none of the lead is removed unless the operation is carried on to a point where soft lead remains. When this point is reached the color of the alkali mass changes and becomes brownish.

The above described reactions express simply what takes place in this process. It is probable, however, that these reactions are somewhat more complicated. As an illustration of what may take place let us consider the case of metallic lead. It is well known that under certain conditions molten sodium nitrate will oxidize molten lead according to the following equation:

4. $Pb+NaNO_3=PbO+NaNO_3$

It appears however that where an alloy containing lead and arsenic, tin or antimony is oxidized by sodium nitrate, especially as in this process, the sodium nitrate acts preferentially upon the arsenic, tin, antimony and lead in the order given. Furthermore, if at any time lead is oxidized through the too rapid addition of sodium nitrate, the lead oxide so formed becomes an oxidizing agent, oxidizing any arsenic, tin or antimony remaining in the metallic state.

I have referred to the use of proper amounts of alkali and oxidizing agent—the amount of oxidizing agent to be used is calculated from the equations given above. The amount of alkali to be used has been experimentally found to be from four to seven times the amount of oxidizing agent, figured as sodium nitrate, used. It is not necessary to bring the alkali mass to any specific condition of pastiness; all that is needed is that it shall be sufficiently pasty to permit easy removal.

The alkali used depends upon the purpose of the treatment. If arsenic and antimony only are to be removed, caustic soda answers all purposes. If tin is to be removed, a mixture of caustic soda and caustic potash is

preferably used—15 parts of caustic potash to 100 parts of caustic soda give very satisfactory results. The function of the caustic potash is to assist in the preferential removal of tin. If caustic soda is used alone for the removal of tin in the presence of antimony, about three parts of tin are removed to one part of antimony. If some caustic potash is present I have found that only 1 part of antimony to 12 parts of tin is removed. The figures given are approximate only but they show clearly how the addition of caustic potash acts to assist the removal, preferentially, of tin instead of antimony.

The process above described relates entirely to the treatment of alloys high in lead for the removal of the arsenic, tin, antimony and other impurities including oxides dissolved in the alloy, and also copper, to the extent that its solubility in the alloy becomes lowered by the removal of arsenic, antimony and tin. After removal from the kettle, the alkali mass is treated for the purpose of recovering in valuable form the arsenic, antimony and tin and other materials contained in it and for the purpose of recovering the alkali for re-use. This treatment is no part of the present invention and can be carried out in any suitable way known to the art.

Claims:

1. The process of purifying lead alloys which consists in maintaining an interface of extended area between a molten mass of such alloy and an overlying mass of caustic alkali containing an oxidizing agent, and coincidently agitating said masses to change the material constituting the contacting faces thereof.

2. The process of removing antimony and also tin and arsenic if present, from lead alloys, which consist in maintaining a horizontal interface of extended area between a molten mass of such alloy and an overlying mass of caustic alkali containing sodium nitrate and coincidentally changing the material constituting the contact faces of the two masses.

3. The process of removing antimony and also tin and arsenic if present, from lead alloys, which consists in maintaining a horizontal interface of extended area between a molten mass of such alloy and an overlying mass of caustic alkali, coincidently changing the material constituting the contact faces of the two masses and gradually adding an oxidizing agent to said materials.

In testimony whereof, I have signed this specification.

GUSTAVE W. THOMPSON.