



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0019 945
A1

⑫

EUROPEAN PATENT APPLICATION

⑪ Application number: 80200322.8

⑤① Int. Cl.³: **C 22 C 1/02, C 22 C 11/02,**
H 01 M 4/68

⑫ Date of filing: 11.04.80

⑤① Priority: 14.05.79 NL 7903764

⑦① Applicant: **SHELL INTERNATIONALE RESEARCH**
MAATSCHAPPIJ B.V., Carel van Bylandtlaan 30,
NL-2596 HR DEN HAAG (NL)

④③ Date of publication of application: 10.12.80
Bulletin 80/25

⑦② Inventor: **Baan, Diederich Jan,** Westervoortsedijk 67d,
NL-6827 AT Arnhem (NL)

⑧④ Designated Contracting States: **AT BE DE FR GB IT NL**

⑦④ Representative: **Keuzenkamp, Abraham et al,** c/o Shell
Internationale Research Maatschappij B.V. P.O. Box 302,
NL-2501 CH 's-Gravenhage (NL)

⑤④ Process for the preparation of calcium and/or strontium-containing lead, lead obtained therewith and battery plates or grids obtained therefrom.

⑤⑦ Process for preparing battery lead containing 100—
900 ppm Ca (or < 2 % Sr) comprises adding less than
100 ppm Mg, which prevents excessive oxidation of Ca.

EP 0 019 945 A1

PROCESS FOR THE PREPARATION OF CALCIUM- AND/OR
STRONTIUM-CONTAINING LEAD, LEAD OBTAINED THEREWITH
AND BATTERY PLATES OR GRIDS OBTAINED THEREFROM

The invention relates to a process for the preparation of lead containing 100-900 ppm calcium and/or an equivalent amount of strontium in which the calcium and/or strontium is added to a lead melt in elemental form, as a compound and/or as an alloy. The main application of calcium-containing lead and of strontium-containing lead is in the form of battery lead. Further, it finds application as cable lead and as anode material in the zinc electrolysis process.

Calcium-and/or strontium-containing lead is usually prepared by melting a lead with a purity of more than 99.9% and by subsequently adding the required alloying elements to the lead melt. This alloying step serves to impart to the lead the desired mechanical properties for battery plates and grids and any other products and also to improve the castability of the lead.

In the past antimony was usually added to the lead. However, antimony causes self-discharge in batteries and it was therefore suggested to replace the antimony by calcium and/or strontium, a change which has met with success. In addition, some tin is often added to the melt and it is also possible to add other desired alloying elements. After the addition of the alloying elements, the molten lead is either made into a half-product or cast directly into the desired end-product. A half-product may consist of ingots which are remelted by the battery manufacturer and are further processed into plates and grids. The half-product may also consist of strip produced by continuous casting and/or rolling, which is further processed into plates or grids by the battery manufacturer.

Both when remelting the half-product and when remelting rejected end-products and also during the considerable period which elapses during the casting of the original melt after alloying, or of the melt obtained by remelting ingots or rejected end-products, the molten lead is in contact with the air.

Now the calcium or strontium content of the melt is found to decrease gradually by oxidation of calcium or strontium, which passes as oxide into the slag layer on top of the melt. Since a certain calcium or strontium content in battery lead is desirable, the diminishing content is found to be very inconvenient. Strontium would usually be required in percentages sufficient to arrive at the desired mechanical properties of the lead and this would normally be less than 2% strontium. It could be partially or totally replaced by calcium of which the influence on the mechanical properties of lead is different. The desired calcium content when calcium is used without any strontium is usually the maximum percentage of calcium soluble in liquid lead at the eutectic temperature (326°C). Unfortunately, it does not suffice to supply more than the desired quantity of calcium during the alloying step in order to anticipate in this manner the expected burning-off of calcium, since the degree of burning-off is difficult to predict (this is also applicable in the case of strontium) and the presence of more calcium in the end products than can be maximally dissolved in liquid lead at the eutectic temperature (326°C) may considerably reduce the corrosion resistance of these products.

In order to solve these problems the present invention proposes to add such an amount of magnesium to the lead melt that less than 100 ppm magnesium is present in the solid lead as prepared. It was surprisingly found that even very low percentages of magnesium in a calcium- or strontium-containing lead melt almost completely inhibit the burning-off of that calcium or strontium. So far no unequivocal explanation for this phenomenon has been found. It is not or at any rate not largely so that the magnesium is sacrificed for the calcium or strontium since in order to prevent a certain quantity of calcium or strontium from being burnt off in a certain period, not a stoichiometric quantity of magnesium is required but a considerably smaller quantity of magnesium is sufficient. Neither does this smaller quantity of magnesium burn off proportionally as rapidly as the calcium or strontium would have done if no magnesium had been present in the

melt. It is possible that the magnesium forms a very thin - protective - oxide skin on the melt which seals the melt off from oxygen.

The maximum solubility of calcium in liquid lead at the
5 eutectic temperature (326°C) is 800 ppm. According to the invention less than 900 ppm of calcium are therefore added while moreover it is preferred to add approx. 700 ppm of calcium... As the result of the magnesium addition it is now sufficient to add the quantity of calcium and/or strontium finally required in the lead.

10 According to the invention - if strontium is used instead of calcium in the lead - less than 2% strontium would normally be required. In order to prevent the burning off of calcium and/or strontium completely or substantially completely during the usual periods for which the melt is liquid, it is usually sufficient to
15 add 1-80 ppm of magnesium.

In the process according to the invention both the calcium and/or strontium and the magnesium can be added in elemental form, in the form of a compound or as an alloy. The percentages given in this specification are all percentages by weight and, where the
20 relevant metal is added in the bound form, they relate to the proportion of that same metal.

In some instances difficulties may be experienced in the addition of the additives to the melt, for example because of the density of the additive (it may float on the lead melt), because
25 of the melting point of the additive (at low melting points fewer difficulties will occur than at higher melting points) or because of the rate at which the additive dissolves in the melt.

These problems may be solved by adding the magnesium in the form of a preliminary alloy or in the form of an intermetallic
30 compound, for example with lead (high density), with aluminium (low melting point) or with calcium or strontium (the problem is halved since only one further additive is required).

If a magnesium-aluminium alloy is added, it is preferred to select an alloy containing 30-70% of magnesium, since these alloys
35 have a melting point near the usual temperature of a lead melt.

An advantage of adding a magnesium-calcium alloy or a magnesium-strontium alloy instead of a magnesium-aluminium alloy is that the corrosion resistance of lead containing magnesium is distinctly higher than that of lead containing an equal quantity of aluminium. Besides, magnesium dissolves in liquid lead more readily than aluminium.

The invention is eminently suitable for those leads which contain tin (usually less than 1%), since tin accelerates the burning-off of calcium-containing lead in a melt, so that in this instance the addition of magnesium is all the more essential.

The exclusive right also pertains to lead obtained with the process according to the invention and to battery plates or grids produced from a lead melt which is obtained in accordance with the invention.

The invention will now be illustrated in greater detail with reference to a number of comparative experiments.

1. A quantity of 700 ppm (0.07%) of calcium was added at 450°C to a quantity of 10 kg of molten lead which contained 0.39% of tin and after some time some samples were taken from the melt. The results obtained are given in Table 1.
2. A quantity of 580 ppm of magnesium and 710 ppm of calcium was added at 450°C to the same quantity of 10 kg of molten lead which contained 0.39% of tin and again after some time some samples were taken. The results are given in Table 1.
3. A quantity of 40 ppm of aluminium and 230 ppm of magnesium as well as 680 ppm of calcium was added at 450°C to the same quantity of 10 kg of molten lead which contained 0.39% of tin. After some time some samples were taken from the melt. The results are given in Table 1.
4. A quantity of 40 ppm of magnesium as well as 700 ppm of calcium was added at 450°C to a similar quantity of 10 kg of molten lead which contained 0.39% of tin and some samples were taken from the melt after some time had passed. The results obtained are given in Table 1.

TABLE 1

Melt		Initial composition		Calcium content in ppm after				
No.	Ca	Al	Mg (in ppm)	30 min.	60 min.	90 min.	120 min.	160 min.
1	700	-	-	500	-	400	400	-
2	710	-	580	710	690	770	720	700
3	680	40	230	650	650	720	650	670
4	700	-	40	700	720	710	690	-

The calcium content was determined with an accuracy of approx. 50 ppm. It can be seen from Table 1 that the calcium content of a melt without magnesium declines rapidly and that addition of magnesium produces a change.

- 5 5. Four melts each of 10 kg of lead which contained 0.39% of tin were prepared to which the following additives were given (analysis of melt as cast):

Melt No. 5: 400 ppm of calcium,

Melt No. 6: 560 ppm of magnesium, 690 ppm of calcium,

- 10 Melt No. 7: 220 ppm of magnesium, 40 ppm of aluminium, 710 ppm of calcium,

Melt No. 8: 20 ppm of magnesium, 690 ppm of calcium.

- 15 These four quantities of lead were each remelted separately after they had been cast and analysed and the quantities of lead thus remelted were again cast and analysed:

Melt No. 5: 230 ppm of calcium,

Melt No. 6: 420 ppm of magnesium, 660 ppm of calcium,

Melt No. 7: 200 ppm of magnesium, 50 ppm of aluminium, 700 ppm of calcium,

- 20 Melt No. 8: 10 ppm of magnesium, 630 ppm of calcium.

This shows that the calcium content of lead decreases by remelting, but that this decrease may be greatly reduced by magnesium.

Melts Nos. 6 and 7 were subsequently again remelted, cast and analysed:

Melt No. 6: 350 ppm of magnesium and 620 ppm of calcium,

Melt No. 7: 170 ppm of magnesium, 50 ppm of aluminium,
690 ppm of calcium.

This shows that even after repeated remelting the quantity of calcium is not greatly reduced if magnesium is present in the lead.

Finally the magnesium- and aluminium-containing quantity of lead (melt No. 7) was again remelted, cast and analysed: 160 ppm of magnesium, 50 ppm of aluminium and 600 ppm of calcium were still present.

This shows that although the quantity of magnesium decreases each time, the quantity of magnesium which remains is such that its effect is adequate.

6. A number of lead/calcium/magnesium/tin alloys containing 0.35% tin were prepared and tested to determine their corrosion resistance behavior:

alloy No.	Ca ppm	Mg ppm	corrosion resistance
1	700	550	very bad
2	700	150	bad
3	700	40	very good
4	800	90	good
5	800	60	very good
6	1200	30	bad

These tests show that a decrease of the magnesium content favours the corrosion resistance and that an increase of the calcium content reduces the corrosion resistance.

7. In order to get an impression of the problems encountered when preparing a binary lead/strontium alloy an amount of 50 grams of strontium was thoroughly stirred through a melt of 11 kg of soft lead at a temperature of 430°C . Subsequently, the strontium content was determined to be 0.20% and

accordingly the efficiency of the strontium addition was only 44%.

8. In order to get an impression of the effect of the measure according to the invention, an amount of 1.15 gram of magnesium and an amount of 23 grams of strontium were thoroughly stirred through a melt of 11.5 kg of soft lead at a temperature of 450°C. Thus 100 ppm magnesium and 0.20% strontium were added to the lead. After stirring the strontium content of the lead was 0.18% and accordingly the efficiency of the strontium addition was 80% now.

9. An amount of 1810 kg of soft lead was melted and at 480°C first 200 grams of magnesium and then 5.5 kg of strontium was added (thus 110 ppm of Mg and 0.30% of Sr were added) and finally 750 grams of aluminium (412 ppm) was added. After thorough stirring a sample of the melt was taken and proved to contain 0.27% strontium (90% efficiency of the strontium addition). The melt was kept at 480°C and subsequent samples were taken after 0.5 hours, 1 hour and 2 hours. The strontium contents thereof were respectively 0.28%, 0.28% and 0.29%. The magnesium content of the last sample was 30 ppm. This suggests that the strontium in the lead melt is protected and can even be redissolved and/or dissolved gradually later on.

C L A I M S

1. A process for the preparation of lead containing 100-900 ppm calcium and/or an equivalent amount of strontium in which the calcium and/or strontium is added to a lead melt in elemental form, as a compound and/or as an alloy, characterized in that such an
5 amount of magnesium is also added that less than 100 ppm magnesium is present in the solid lead as prepared.
2. A process as claimed in claim 1, characterized in that less than 2% strontium is added.
3. A process as claimed in claim 1, characterized in that
10 approx. 700 ppm of calcium is added to the lead melt.
4. A process as claimed in any one of claims 1-3, characterized in that 1-80 ppm of magnesium is added.
5. A process as claimed in any one of claims 1-4, characterized in that the magnesium is added in the form of a compound or alloy.
- 15 6. A process as claimed in claim 5, characterized in that a magnesium-aluminium alloy is added.
7. A process as claimed in claim 5, characterized in that a magnesium-calcium alloy or a magnesium-strontium alloy is added.
8. A process as claimed in claim 6, characterized in that an
20 alloy containing 30-70% of magnesium is added.
9. A process as claimed in any one of claims 1-8, characterized in that less than 1% of tin is also added.
10. Lead obtained with the process as claimed in any one of the preceding claims.
- 25 11. Battery plates or grids obtained from a lead melt obtained with the process as claimed, in any one of claims 1-9.



European Patent
Office

EUROPEAN SEARCH REPORT

0019945
Application number

EP 80 20 0322

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ¹)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>US - A - 2 306 899</u> (PHILLIPS et al.) * Claim 1 * --	1,3,4,9	C 22 C 1/02 C 22 C 11/02 H 01 M 4/68
	<u>GB - A - 499 549</u> (AMERICAN SMELTING AND REFINING CY.) * Claims 1,2,3 * --	1,9,10,11	
A	<u>DE - C - 323 852</u> (UNITED LEAD CY.) * Claim 1; page 2, example 7, lines 11-13; page 1, example 4, lines 59-64 * --	1,2	TECHNICAL FIELDS SEARCHED (Int.Cl. ³)
A	<u>US - A - 3 920 473</u> (SIMS et al.) * Claims 1-4 * --	1,11	C 22 C 11/02 C 22 C 1/02 H 01 M 4/68
A	<u>GB - A - 1 414 171</u> (JOSEPH LUCAS (BATTERIES) LTD) * Claims 1,2,4 * --	1,11	
A	<u>DE - A - 2 611 575</u> (METALLGESELLSCHAFT A.G.) * Claim 1 * --	1,11	CATEGORY OF CITED DOCUMENTS
P	<u>DE - A - 2 921 290</u> (CHLORIDE GROUP LTD.) * Claims 1,3,4,6,7,8,9 * ----	1,2,4,9,10,11	X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons &: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 22-07-1980	Examiner LIPPENS