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D E C I S I O N
of 13 March 2002

Case Number: T 0166/99 - 3.2.2

Application Number: 89305122.7

Publication Number: 0343012

IPC: C22B 13/08

Language of the proceedings: EN

Title of invention:

Magnesium-calcium alloys for debismuthizing lead

Patentee:

TIMMINCO LIMITED

Opponent:

Pechiney Service Brevets

Headword:

-

Relevant legal provisions:

EPC Art. 56

Keyword:

"Inventive step (yes) after amendment"

Decisions cited:

-

Catchword:

-



Case Number: T 0166/99 - 3.2.2

D E C I S I O N
of the Technical Board of Appeal 3.2.2
of 13 March 2002

Appellant: Pechiney
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Representative: Powell, Stephens David
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Decision under appeal: Decision of the Opposition Division of the
European Patent Office posted 18 December 1998
rejecting the opposition filed against European
patent No. 0 343 012 pursuant to Article 102(2)
EPC.

Composition of the Board:

Chairman: W. D. Weiß
Members: R. Ries
J. C. M. de Preter

Summary of Facts and Submissions

- I. European patent No. 0 343 012 was granted on 13 September 1995 on the basis of European patent application No. 89 305 122.7.
- II. The granted patent was opposed by the present appellant (Pechiney) on the grounds that its subject matter lacked an inventive step with respect to the state of the art (100(a) EPC).
- III. With its decision posted 18 December 1998 the Opposition Division held that the patent could be maintained as granted and rejected the opposition. In the opposition proceedings, inter alia the following documents were cited:
- E1: US-A-2 129 445
- E2: Transactions AIME-Journal of Metals, March 1956, Davey, T.R.A., "Debismuthizing of Lead", pages 341 to 350
- IV. An appeal was lodged against this decision on 9 February 1999.
- V. In an official communication, the Board referred to the documents
- E3: D. Evers: "Die Entwismuthisierung nach dem Kroll-Betterton-Verfahren", Erzmetall, Zeitschrift für Erzbergbau und Metallhüttenwesen, Band II, (1949), Seiten 129 bis 133
- E4: Ullmanns Encyclopädie der technischen Chemie,

volume 8, Verlag Chemie, Weinheim, (1974),
page 570

VI. In its response to this communication, the patentee referred to document

E6: FR-A-2 514 786

and submitted Declarations of Dr W.D. MacDonald and Mr Philip Moor, respectively.

VII. Oral proceedings were held before the Board on 13 March 2002.

The appellant (opponent) requested that the decision under appeal be set aside and the patent be revoked.

The respondent (proprietor of the patent) requested that the patent be maintained in amended form on the basis of the following documents:

Claims: 1 to 7 as submitted at the oral proceedings

Description: pages 3, 7 and 8 according to the patent specification;
pages 4 to 6 appended to the decision under appeal as auxiliary request;

Figures: as granted.

Independent claims 1 and 4 of the main request read as follows:

"1. The use of an alloy for the removal of bismuth and

other impurities from lead, characterized in that the alloy consists essentially of magnesium and calcium, the magnesium being present in the proportion of from 65% to 75% on a weight basis, the alloy being added to the lead bath at a temperature in the range of from 415 to 500°C."

"4. A method for removing bismuth and other impurities from an impurity containing lead bath, which method comprises the steps of: providing an alloy consisting essentially of magnesium and calcium having a proportion of magnesium from 65% to 75% on a weight basis; adding said alloy to a lead bath at a temperature of approximately 415°C to 500°C so that solid alloy remains in the lead bath, and permitting the solid alloy to dissolve in the lead, said alloy containing the only calcium being added to the bath; cooling said lead bath to a temperature just above its liquidus temperature; and recovering the magnesium and calcium in association with impurities from the lead bath."

VIII. The appellant argued as follows:

The technical background describing the Kroll-Betterton process for debismuthizing lead is described by document E3 which recommends the simultaneous addition of magnesium and calcium to a lead bath containing bismuth. For a typical initial content of about 0.1% Bi in the Pb-bath, the amounts of Mg and Ca which are necessary to precipitate bismuth in the form the intermetallic compound Bi_2CaMg_2 can be calculated according to the formula given on page 133, first paragraph, right hand column of document E3. This calculation always leads to a Mg-Ca composition having

a ratio of about 2/3 Mg and 1/3 Ca, or - put the other way - of a chemically most effective mixture comprising about 65% Mg and 35% Ca. Document E3 further proposes the addition of this composition in the form of pure magnesium in combination with a Pb-Ca4.5% alloy rather than to supply both components in the form of a Mg-Ca alloy to the bath as claimed in the opposed patent. However, the same ratio and quantities of Mg and Ca are needed, irrespective of how they are added to the lead bath. Moreover, replacing a mixture of two components by an alloy comprising these elements merely represents common metallurgical practise which is always resorted to if one or both components in the pure form are highly reactive, exhibit a high melting point or high vapour pressure or if they are even explosive at the process temperature. For example CaSi alloys are used in ferrous metallurgy whereby the high reactivity and vapour pressure of pure calcium is significantly reduced by alloying it with silicon so that this alloy can be safely stored and added to liquid steel. A similar effect can be expected when alloying Mg with Ca. The widely known Ca-Mg phase binary diagram (Figure 1 in the patent) shows a Ca-rich and a Mg-rich eutecticum and a stable intermetallic compound Mg_2Ca at about 45% Ca/55% Mg. Since the compositions on the Ca-rich side of the phase diagram always comprise Mg_2Ca plus highly reactive elemental calcium and given that - according to the teaching in document E3 - a 65%Mg-35%Ca composition is most effective for debismuthizing lead, the metallurgist is prompted to work on the magnesium rich side of the phase diagram. In doing so, the presence of highly reactive pure calcium in the Mg-Ca alloy is avoided and the favourable 65% Mg-35% Ca composition can be selected which exactly corresponds to preferred alloy compositions claimed in claim 2 of

the patent. Moreover, the use of Ca-Mg alloys for debismuthizing lead was already known in the art, for instance from document E1 which discloses the addition of Ca and Mg in the form of an 20.6Ca-Mg alloy. Also document E6 proposes to add both elements in the form of granules consisting of an Ca-Mg alloy (see E6, claim 1). Consequently, the use of the Ca-Mg alloy according to claim 1 of the opposed patent is obvious for the metallurgist by combining the technical teaching of documents E3 and E6 or E1, respectively.

This statement also applies to independent claim 4, which merely comprises trivial technical features such as dissolving the Mg-Ca alloy in the lead bath held at the temperature of 415 to 500°C that is typical for the Kroll-Betterton process, cooling the bath and recovering the magnesium and calcium in association with impurities from the lead. Hence, the subject matter of process claim 4 does not involve an inventive step either.

XI. The respondent argued as follows:

The Kroll-Betterton process for debismuthizing lead is amply described by documents E2 (Davey) and E3 (Evers). In spite of the persisting requirement of avoiding the employees' exposure to lead vapours and reducing the costs of the reagents, the basic principle of the debismuthizing process has remained unchanged over the last 60 years. The reagents have been added in the form of essentially pure Mg as sticks and Ca as an alloy in lead comprising 2 to 5% Ca (see E2, page 346, left hand column, 2nd paragraph and E3, page 130, right hand column, paragraph 1). However, using Ever's formula given on page 133 of E3 would imply preparing a

different composition of Mg and Ca for each batch of lead. Moreover, given that the preparation of a Mg-Ca alloy is associated with an increase of cost, a general prejudice existed to do so, the more so since nothing is mentioned in E2 or E3 pointing to a significant benefit that could come from using these alloys. It also could not be expected or predicted that a MgCa alloy would be less reactive than the pure components.

Document E1 mentions the debismuthizing of lead by floating a 79.4%Mg-20.6%Ca alloy on the surface of a mechanically stirred lead bath but this process necessitates operation at 593°C (1100°F) compared to about 380-500°C used in the Betterton-Kroll process. Therefore, this process has never been applied on an industrial scale.

Another attempt at using Ca-Mg alloys for debismuthizing lead was made by document E6 (Extramet) which however proposes two types of granules, one comprising a CaMg alloy near the calcium-rich eutectic point and the second alloy comprising a composition near the magnesium rich eutectic point.

Neither E1 nor E6 envisage the use of the MgCa alloy composition claimed in the patent or make it appear obvious to do so. On the contrary, inventive research and experimental work was necessary to determine the compositional range of CaMg alloys which effectively avoid flaring, which are stable in the ordinary atmosphere and which dissolve sufficiently readily and chemically effectively in the lead bath at normal Kroll-Betterton temperatures. Hence, the claimed use and process involved an inventive step.

Reasons for the Decision

1. The appeal is admissible.

2. *Amendments*

According to amended claim 1 the use of the MgCa alloy has been restricted to a lead bath held at between 415°C and 500°C. This temperature range is typical for the Kroll-Betterton process and finds ample support in the patent specification, e.g. in method claim 4 or on page 5, lines 17, 18. The amendments to the description pages 4 to 6 are a restriction of the Mg to Ca ratio to the preferred range of 1.0 to 3.0. Hence the amendments satisfy the requirements of Article 123 EPC.

3. *Novelty*

None of the cited documents discloses the use of a MgCa alloy comprising 65 wt% to 75 wt% Mg for the removal of bismuth from a lead bath held between 415 to 500°C. In particular, the 20.6Ca-79.4Mg alloy mentioned in document E1 and the individual CaMg16 and MgCa18 eutectic compositions referred to on page 3, paragraph 1 of document E6 fall outside the claimed range. A further difference between the prior art and the use of the claimed MgCa alloys resides in that the alloys known from documents E1 and E6 are added to the lead bath at a significantly higher temperature (E1: 1100°F = 593°C; E6, page 3, second paragraph: 520 to 600°C). The remaining documents E2, E3 mention that magnesium and calcium (generally in the form of a PbCa alloy) are added separately to the lead bath.

Consequently, the use according to claim 1 and the process according to claim 4 is novel. Since the novelty of the claimed subject matter was not disputed at the oral proceedings, there is no need to deal with this issue in more detail.

4. *The closest prior art*

The patent at issue relates to the use of calcium-magnesium alloys for removing bismuth from lead by the Kroll-Betterton process which is generally operated between 380 and 500°C (cf. the patent specification page 3, lines 3 to 16; page 4, lines 5 to 7; page 6, lines 29 to 33). This process which is described in detail in document E3 takes advantage of the extremely low solubility of the intermetallic compound CaMg_2Bi_2 that is allowed to precipitate upon cooling the lead bath to about 380°C. To this end, a heterogeneous mixture of magnesium (pure) and calcium (as Pb-Ca alloy) is added to the bath whereby -according to the formula given on page 133 right hand column of document E3 - the additive should have the integral composition of about 65wt% Mg- 35wt Ca for optimum chemical effectiveness (cf. also E3, page 131, column 2, lines 15 to 12 from the bottom; page 132, first column, first and second full paragraph; page 132: Bemerkungen zu den Grundlagen des Verfahrens). The technical information relating to the Kroll-Betterton process which is given in document E2, page 347, left hand column does not go beyond that disclosed in document E3. Therefore, document E3 represents the closest prior art.

5. *Problem and solution*

Given that the reactive alkaline earth metals are prone to excessive atmospheric oxidation, the addition of magnesium and calcium to the lead bath according to the Kroll-Betterton process entails the drawbacks of bright flaring, excessive fume generation and the overall loss of reagent. This leads to lower reagent recoveries, higher processing cost, unpredictable final bismuth levels and to serious environmental concerns.

Starting from this prior art represented by document E3, the problem underlying the opposed patent, therefore, resides in providing a process which minimizes or even avoids the above mentioned disadvantages. Moreover, the reagents should be in a form which does not require special packaging or a protective atmosphere to prevent oxidation, is sufficiently strong to enable casting and shipping, dissolves rapidly in a lead bath at conventional temperatures and allows minimumisation of the amounts of reagents required for removing bismuth.

According to claim 1 of the patent at issue, this problem is solved by using a (65-75%)Mg-Ca **alloy** rather than the heterogeneous mixture of two separate components as proposed by the prior art. The laboratory test results summarized in Table 1 of the patent specification and the Examples 1 to 4 confirm that by using the claimed magnesium-calcium alloys at temperatures between 415 and 500°C for debismuthizing lead, excessive atmospheric oxidation of the additives, flaring or fume generation is effectively avoided.

6. *Inventive step*

6.1 It has been agreed by the all parties that the

chemically most effective Mg-Ca composition for debismuthizing lead is already known in the art, e.g. from document E3. Crucial to the question of inventive step is, therefore, to examine whether the addition of the reagents in the form of the claimed MgCa alloy was obvious from the prior art.

- 6.2 As set out above, document E3 does not given any hint to the expert that - compared to the conventional practice of adding Mg and Ca separately - any beneficial effect upon the recovery and performance of magnesium and calcium could be expected by using these reagents in the form of a MgCa alloy and neither does document E2. Like E3, this document also teaches to add separately (pure) magnesium as sticks and calcium as an alloy in lead containing 2 to 5% Ca (cf. page 347, first column, second paragraph).
- 6.3 It is only in documents E1 and E6 that a MgCa pre-alloy actually has been envisaged to be used for the removal of bismuth from lead. To this end, document E1 proposes one singular alloy composition consisting of 20.6%Ca-79.4%Mg which can be floated on the lead bath but this alloy composition falls outside the elemental ranges stipulated in the patent at issue (cf. E1, page 5, second column, lines 29 to 59). Having regard to the high liquidus temperature of the 20.6Ca/79.4Mg alloy which is - according to the known binary phase diagram - about 580°C, it is indispensable to raise the temperature of the lead bath to 1100°F (593°C) so that the alkaline earth metal alloy dissolves quickly and effectively in the bath (cf. E1, page 6, first column, lines 3 to 18). The temperature of 593°C is, however, far above any realistic operation regime. Moreover, the final bismuth content in the lead after purification

appears to remain at an unacceptable high level (according to Example 6 the final bismuth content is 0.45%). For these reasons, there was agreement between the parties at the oral proceedings that the process disclosed in document E1 has not been applied commercially. In view of these considerations, the teaching given in document E1 is pointing away from putting into practise this process, either from using the 79.4%Mg-20.6%Ca alloy at low temperatures of 500°C or below, or more importantly, from using in the Kroll-Betterton process other MgCa alloys exhibiting even higher liquidus temperatures than the alloy selected in E1.

- 6.4 According to the teaching of the remaining document E6, the low recovery of calcium and magnesium, when supplied separately to the lead bath, can be improved by adding the alkaline earth metals in the form of a mixture of granules which (in the overall composition) consist of 50-80%Mg/Ca alloy, or more preferably, of a 55-75%Mg/Ca alloy (cf. E6, page 2, second and fourth paragraph). However, in order to cope with the relatively high liquidus temperatures of these alloys and in order to increase the dissolving rate in the lead bath, document E6 proposes the use of two separate types of granules comprised of different alloys: for the first type of granules, the high magnesium eutectic composition (Mg-16.2%Ca; $T_m=517^\circ\text{C}$) is selected, and the second type of granules consists of the calcium rich eutectic composition (Mg-82%Ca; $T_m=445^\circ\text{C}$) which both fall outside the compositional ranges claimed in the patent at issue (cf. E6, page 2, last paragraph to page 3, first paragraph). As is further disclosed in document E6, page 3, second paragraph, this mixture of granules is added to a lead bath held at a temperature

between 520 to 600°C in order to guarantee satisfactory dissolving rates. Thus, as in E1, also the process described in document E6 needs to be operated at temperatures far above those which are used in the conventional Kroll-Betterton process. Although document E6 takes advantage of adding Ca and Mg to molten lead in the form of MgCa-alloys to safeguard against a low recovery, it represents a technical approach to the problem of debismuthizing lead that is different and contrary to that stipulated in the patent at issue since E6 advocates to use a mixture of granules composed of two different low-melting MgCa alloys rather than a single alloy. Nothing can be found in document E6 inciting a skilled person to use only one single high melting MgCa alloy instead of two eutectic MgCa-alloys and thus to act against the teaching given in this document. Moreover, it cannot be deduced from document E6 that a quick and effective removal of bismuth from the molten lead can be achieved simply by floating and dissolving the claimed high melting MgCa-alloy in a lead bath held at conventional temperatures between 415 and 500°C, ie. without significantly increasing the temperature of the lead bath.

- 6.5 It is true that the binary Mg-Ca phase diagram includes the stable intermetallic compound Mg_2Ca which appears appropriate to reduce the high reactivity of pure calcium. However, the physical and chemical properties of such intermetallic compounds are not predictable simply by looking at the phase diagram. According to the patentee, tests have shown that Mg_2Ca per se is still highly reactive with oxygen, disintegrates at increasing temperatures and cannot be stored without protection. In view of these findings, the acceptable amount of calcium (and therefore the amount of Mg_2Ca) in

the alloy used in the patent is restricted to 35% at maximum to provide an excellent match in the desired physical and chemical properties of the alloy mentioned above.

7. Consequently, the subject matter of use claim 1 and also of method claim 4 involves an inventive step vis-à-vis the cited prior art.
8. The dependent claims 2 and 3 as well 5 to 7 relate to preferred embodiments of claims 1 and 4, respectively, and are, therefore, equally allowable.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.
2. The case is remitted to the first instance with the order maintain the patent in amended form on the basis of the following documents:

Claims: 1 to 7 as submitted at the oral proceedings;

Description: pages 3, 7 and 8 according to the patent specification
pages 4, 5 and 6 as appended to the decision under appeal as auxiliary request;

Figures: as granted.

The Registrar:

The Chairman:

V. Commare

W. D. Weiß