

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Process of Treating Amalgams of Metals which are Difficultly Soluble in Mercury

5 We, SIEMENS & HALSKE GESELLSCHAFT M.B.H., an Austrian Company of 12, Apostelgasse, Vienna III, Austria, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process of treating amalgams of metals which are difficultly soluble in mercury.

15 In this specification the term "metal" has the meaning "metals other than mercury" and the phrase "difficultly soluble" includes the meaning of "insoluble".

It is a main object of the invention to reduce the amount of energy required for the recovery of metals which are difficultly soluble in mercury from dilute amalgams.

20 It is another object of the invention to provide a process of conditioning a dilute amalgam of a metal which is difficultly soluble in mercury for separation of the mercury therefrom in the liquid phase to a concentration of said metal which was previously achievable only by distilling the mercury.

25 It is another object of the invention to provide an improved process of separating metals which are difficultly soluble in mercury from their amalgams by a superficial oxidation of said metals.

Other objects and advantages of the invention will become apparent as the specification proceeds.

35 In amalgam metallurgy, metallic mercury is used as an auxiliary substance in the recovery of metals. The amalgam-metallurgical recovery of such metals always proceeds in two stages. In the first stage the corresponding metal amalgams are formed, e.g., by direct electrolysis, by phase exchange reactions with less noble amalgams and the aqueous metal salt solutions, by the reduction of metal compounds with the aid of reducing amalgams, and  
40 by other methods. In the second stage the metal to be recovered must be separated from

the mercury with which it is amalgamated. Metals which are difficultly soluble in mercury may preferably be recovered from their amalgams by distilling the readily volatile mercury. 50 Although the latent heat of vaporization of mercury is small, a certain amount of energy can still be saved during the low-temperature distillation if amalgams of the highest possible concentration are subjected to distillation. The known amalgamating reactions generally give 55 amalgams having concentrations of no more than two percent by weight. Amalgams containing 1—2% by weight of metals which are difficultly soluble in mercury have a highly viscous to pasty consistency. However, such amalgams may be enriched to a content of, at most, 10 percent by weight of metal in mercury by simple known liquid-solid separation processes such as filtering, centrifuging, ferromagnetic separation. All these processes give a 60 mercury which is almost free of metal and a stiff amalgam paste of butterlike consistency. No processes have been known before which enable a more effective separation with such simple means. Therefore, the material subjected to the previously known low-temperature distillation processes consisted always of amalgams of relatively low concentration, containing between 0.5% and 5% to a maximum 65 of 10% by weight of metal. By way of example it may be stated that a 1% iron amalgam obtained by direct electrolysis could not be enriched by filtration to an iron content of more than 10 percent iron even under very high pressures (70kg./sq. cm.). This 10% iron amalgam has already a friable consistency and is no longer capable of flowing. 70

It is also known that amalgams having a small content of metals which are very difficultly soluble in mercury can be aged to some degree by prolonged storage. Enriched amalgams containing up to as much as 5—10% metal can then be obtained by filtering aged amalgams. More highly enriched amalgams 75 obtained without distillation of the mercury have not been disclosed so far. It has already

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been disclosed to age amalgams at an elevated temperature in order to facilitate the floating of the metal particles that are insoluble in mercury. This measure, however, does not lead to a further enriching of the metal in the amalgam.

It has been found that heating of amalgams under superatmospheric pressure above 360° C. preferably above 450° C. without any distillation of mercury results in such a coarsening of the grains of the metal which is difficultly soluble in the mercury that highly concentrated amalgams result from the subsequent separation of the major portion of the liquid mercury by known methods, e.g. by filtration. These metal amalgams contain 15—50% metal. Surprisingly it has been found that the heating of the amalgams above 360° C. preferably above 450° C. at a pressure which is equal to or higher than the vapour pressure of the mercury which corresponds to this temperature, whereby the vapourization of the mercury is prevented, results in such a coarsening of the grain that the amalgams contain in all cases more than 25% metal. The residual mercury may be removed in a manner known *per se* by distillation. This process step alone enables a saving of 50—90% of the energy used for low-temperature distillation. The super-atmospheric pressure required during the heat treatment of the amalgam may be produced by heating the amalgam above the boiling point of mercury in a pressure-tight chamber so that the heated amalgam is subjected to the vapor pressure of the mercury. If the heat treatment is carried out in a continuous operation the incoming and outgoing amalgams may be subjected to counterflow heat exchange with each other for preheating the incoming amalgam and cooling the outgoing amalgam. In this case the heat-treating chamber may be sealed with liquid amalgam at the feed and discharge ends. The process according to the invention may be illustrated by the following examples:—

#### EXAMPLE 1.

Iron amalgam containing 0.3% iron was heated for five minutes under pressure at 550° C. and filtered after cooling. The filtration residue contained 32% iron whereas the mercury filtrate was free of iron. The filtration residue had the same consistency (butterlike paste) as iron amalgam obtained after filtration with an iron content of 3% if the starting amalgam had not been heat-treated under pressure.

#### EXAMPLE 2.

Nickel amalgam containing 4% nickel was heated under pressure for five minutes at 550° C. Filtration after cooling gave a pasty filtration residue containing 31% nickel.

#### EXAMPLE 3.

The same nickel amalgam as in Example 2

was treated for one hour at 440° C. Filtration at room temperature gave a residue containing 20% nickel and having almost the same consistency as that obtained in Example 2.

#### EXAMPLE 4.

Copper amalgam containing 3.5% copper was treated for 15 minutes at 530° C. The filtration residue contained 30% copper.

#### EXAMPLE 5.

A manganese amalgam containing 1.8 percent by weight of manganese was treated at 560° C. for 30 minutes and filtered in the cold. The filtration residue contained only 11% manganese.

#### EXAMPLE 6.

The same manganese amalgam as in Example 5 was treated at 560° C. for 30 minutes and filtered at 280° C., at a temperature below the boiling point of mercury. The filtration residue contained 35 percent manganese.

The application of higher temperatures during the heat treatment may increase the concentration of metal in the filtration residue to as much as 50 percent. In practice, however, 600° C. will not be greatly exceeded because the vapor pressure of mercury increases with temperature to such a degree that its control under commercial conditions becomes difficult.

The present invention includes an additional important feature which consists in enriching the metal content of amalgams by oxidation. The effect described is most easily observed with chromium amalgam which will separate into a gray chromium powder and chromium-free mercury after a short period of standing in the air. Iron amalgam must be allowed to stand in the air for several days or even weeks to effect this separation. The iron which has been separated in this way from the mercury with which it had been amalgamated has already been investigated. It was found to consist of metallic iron having a radiologically amorphous oxide layer or oxygen covering layer, which eliminates the wettability of these iron particles by mercury. Previous attempts to commercially utilize this effect for the removal of mercury from metal amalgams have remained without any practical success because this separation is not completed even within very long time, particularly with those amalgams which are of commercial interest (amalgams of iron, nickel, manganese, copper and others).

Surprisingly it has been found that the amalgams which have been enriched according to the invention by filtering dilute amalgams after a heat treatment, are under the conditions now to be described particularly suitable for oxidative separation. It has been found that this oxidative separation of amalgams which had been treated at elevated temperature under pressure will occur particularly

quickly and completely if the mercury contains a small amount of a metal which has a higher affinity to oxygen than the metal to be recovered from the amalgam and which is at least partly soluble in mercury. For the effect of the oxidative separation it is of minor importance whether this metal of higher affinity to oxygen is added to the mercury before the heat treatment (under pressure) or after the heat treatment (under pressure) before the oxidation. Aluminium, e.g., has proved particularly suitable as an addition to heat-enriched amalgams to promote their oxidative separation. It has been found that an addition of  $10^{-4}$  to  $10^{-2}$  percent by weight of aluminium, related to the mercury, has a particularly desirable effect. An addition of manganese in an order of  $10^{-3}$  to  $10^{-1}$  per cent by weight is also suitable. Manganese is preferably incorporated in the amalgam by a direct electrolysis of a manganese-containing iron salt solution. To incorporate aluminium, it may be dissolved in mercury at elevated temperatures or may be added to the mercury before the heat treatment under pressure. It has been found that the separation depends to a high degree on the residence time of the amalgam in the pressurized heat-treating zone after an addition of aluminium. The following example illustrates the enriching effect on iron amalgam to which traces of aluminium had been added before the heat treatment:—

#### EXAMPLE 7.

Iron amalgam having an iron content of 2.5% was heat-treated for ten minutes at 550° C. under pressure and was then filtered. In this and the following three examples, the access of air causes the filter cake containing initially 15—50% metal to disintegrate into a metal powder having a low mercury content and into metal-free mercury, which drains through the filter. In Example 7, a separation to as much as 85 per cent by weight of metal was possible on filtration.

#### EXAMPLE 8.

When the same iron amalgam as in Example 7 was heat-treated for two hours, it was possible to enrich it by filtration only to as much as 60 percent by weight of metal.

#### EXAMPLE 9.

When the same amalgam as in Examples 7 and 8 was heat-treated for four hours, it was possible to enrich it by filtration only to as much as 40 percent by weight of metal.

#### EXAMPLE 10.

When the same amalgam as in Examples 7 to 9 was heat-treated for five hours, it was possible to enrich it by filtration only to as much as 32 per cent by weight of metal. A separation into iron powder and iron-free mercury was not effected.

This behavior may be due to a reaction of the mercury-dissolved aluminium with the iron during the heat treatment. When the aluminium has been combined with the iron which is dispersed in the mercury it is no longer available for conveying oxygen through the mercury to the iron particles to effect the oxidative separation. It has been found satisfactory, therefore, to add the oxygen transmitting agent to the mercury after the pressure treatment. To this end, aluminium may be dissolved in mercury at 500° C. and the resulting aluminium amalgam may be admixed in the cold to the pressure-treated iron amalgam.

The metal powder obtained by oxidative separation is not actually oxidized but has only an oxygen covering on the several metal grains. It is suitable as a starting product for sintered bodies.

#### WHAT WE CLAIM IS:—

1. A process of treating an amalgam containing less than 10 percent by weight of a metal which is difficultly soluble in mercury, which comprises heating said amalgam above 360° C. at a pressure which is equal to or higher than the vapour pressure of Hg at the operating temperature to condition said amalgam for a separation of mercury therefrom in the liquid phase.

2. A process as set forth in Claim 1, which is applied to an amalgam which contains 0.5—5 percent by weight of said metal.

3. A process of treating an amalgam containing less than 10 percent by weight of a metal which is difficultly soluble in mercury, which comprises heating said amalgam above 450° C. at a pressure which is equal to or higher than the vapour pressure of Hg at the operating temperature to condition said amalgam for a separation of mercury therefrom in the liquid phase.

4. A process of enriching an amalgam containing less than 10 percent by weight of a metal which is difficultly soluble in mercury, which comprises heating said amalgam above 360° C. at a pressure which is equal to or higher than the vapour pressure of Hg at the operating temperature and then separating mercury in the liquid phase from said amalgam to obtain a residual amalgam enriched with said metal.

5. A process as set forth in Claim 4, which is applied to an amalgam which contains 0.5—5 percent by weight of said metal.

6. A process of enriching an amalgam containing less than 10 percent by weight of a metal which is difficultly soluble in mercury, which comprises heating said amalgam above 450° C. at a pressure which is equal to or higher than the vapour pressure of Hg at the operating temperature and then separating mercury in the liquid phase from said amalgam to obtain a residual amalgam enriched with said metal.

7. A process of recovering a metal which is difficultly soluble in mercury from an amalgam containing less than 10 percent by weight of said metal, which comprises heating said amalgam above 360° C. at a pressure which is equal to or higher than the vapour pressure of Hg at the operating temperature, then separating mercury in the liquid phase from said amalgam to obtain a residual amalgam enriched with said metal, and removing mercury from said residual amalgam.

8. A process as set forth in Claim 7, in which mercury is distilled from said residual amalgam.

9. A process as set forth in Claim 7, in which mercury is removed from said residual amalgam by oxidising the difficultly soluble metal contained in said residual amalgam to form an oxide-covered amalgam powder and mercury which is substantially free of said difficultly soluble metal, and separating said amalgam powder from said mercury.

10. A process as set forth in Claim 9, in which mercury is distilled from said amalgam powder.

11. A process of recovering a metal which is difficultly soluble in mercury from an amalgam containing less than 10 percent by weight of said metal, which comprises heating said amalgam above 360° C. at a pressure which is equal to or higher than the vapour pressure of Hg at the operating temperature, then separating mercury in the liquid phase from said amalgam to obtain a residual amalgam enriched with said metal, adding to said amalgam at any time before said separation of mercury a metal which has a higher affinity to oxygen than said difficultly soluble metal and which is at least partly soluble in mercury, allowing said difficultly soluble metal in said residual amalgam to oxidize to form an oxide-covered amalgam powder and mercury which is substantially free of said difficultly soluble metal, and separating said amalgam powder from said mercury.

12. A process as set forth in Claim 11, in which said metal of higher affinity consists of aluminium and is added in an amount of  $10^{-4}$  to  $10^{-2}$  percent by weight related to the mercury contained in said amalgam.

13. A process as set forth in Claim 11, in which said metal of higher affinity consists of manganese and is added in an amount of  $10^{-3}$  to  $10^{-1}$  percent by weight related to the mercury contained in said amalgam.

14. A process as set forth in Claim 11, in which mercury is distilled from said separated amalgam powder.

15. A process of recovering a metal which is difficultly soluble in mercury from an amalgam containing less than 10 percent by weight of said metal, which comprises heating said amalgam above 360° C. at a pressure which is equal

to or higher than the vapour pressure of Hg at the operating temperature, then adding to said amalgam a metal which has a higher affinity to oxygen than said difficultly soluble metal and which is at least partly soluble in mercury, thereafter separating mercury in the liquid phase from said amalgam to form a residual amalgam enriched with said difficultly soluble metal, allowing said difficultly soluble metal in said residual amalgam to oxidize to obtain an oxide-covered amalgam powder and mercury which is substantially free of said difficultly soluble metal, and separating said amalgam powder from said mercury.

16. A process of recovering a metal which is difficultly soluble in mercury from an amalgam containing less than 10% by weight of said metal, which process comprises adding to said amalgam a metal which has a higher affinity to oxygen than said difficultly soluble metal and which is at least partly soluble in mercury, then heating said amalgam above 360° C. under a pressure which is equal to or higher than the vapour pressure of mercury at the operating temperature, thereafter separating mercury in the liquid phase from said amalgam to obtain a residual amalgam enriched with said difficultly soluble metal, allowing said difficultly soluble metal in said residual amalgam to oxidize to form an oxide-covered amalgam powder and mercury which is substantially free of said difficultly soluble metal, and separating said amalgam powder from said mercury.

17. A process of treating an amalgam containing less than 10 percent by weight of a metal which is difficultly soluble in mercury, substantially as described hereinbefore.

18. A process of recovering a metal which is difficultly soluble in mercury from an amalgam containing less than 10 percent by weight of said metal, substantially as described hereinbefore.

19. An amalgam containing less than 10 percent by weight of a metal which is difficultly soluble in mercury, whenever produced by a process as claimed in any of Claims 1 to 3 and 17.

20. An amalgam of a metal which is difficultly soluble in mercury, whenever produced by a process as claimed in any of Claims 4 to 6.

21. Metal which is difficultly soluble in mercury, whenever recovered from its amalgam by a process as claimed in any of Claims 7 to 16 and 18.

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