



HU000028982T2

(19) **HU****MAGYARORSZÁG**
Szellemi Tulajdon Nemzeti Hivatala(11) Lajstromszám: **E 028 982**(13) **T2****EURÓPAI SZABADALOM**
SZÖVEGÉNEK FORDÍTÁSA(21) Magyar ügyszám: **E 14 780620**(22) A bejelentés napja: **2014. 09. 15.**

(96) Az európai bejelentés bejelentési száma:

EP 20140780620

(97) Az európai bejelentés közzétételi adatai:

EP 2895287 A1 **2015. 04. 16.**

(97) Az európai szabadalom megadásának meghirdetési adatai:

EP 2895287 B1 **2016. 07. 13.**(51) Int. Cl.: **B22F 1/00**

(2006.01)

C22C 1/04

(2006.01)

C22C 9/02

(2006.01)

C22C 30/02

(2006.01)

C22C 30/06

(2006.01)

H01J 7/18

(2006.01)

H01J 7/20

(2006.01)

H01J 93/95

(2006.01)

H01J 61/28

(2006.01)

(86) A nemzetközi (PCT) bejelentési szám:

PCT/IB 14/064523

(87) A nemzetközi közzétételi szám:

WO 15052604

(30) Elsőbbségi adatok:

MI20131658**2013. 10. 08.****IT**

(73) Jogosult(ak):

Saes Getters S.p.A., 20020 Lainate (MI) (IT)

(72) Feltaláló(k):

CORAZZA, Alessio, I-22100 Como (CO) (IT)**DI GIAMPIETRO, Diego, I-65122 Pescara (PE) (IT)****SANTELLA, Gianni, I-67049 Tornimparte (AQ) (IT)**

(74) Képviselő:

**Danubia Szabadalmi és Jogi Iroda Kft.,
Budapest**(54) **Anyagkeverék higanyt leadó berendezésekhez és ilyen anyagkeveréket tartalmazó berendezések**

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.



(11) **EP 2 895 287 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
13.07.2016 Bulletin 2016/28

(21) Application number: **14780620.2**

(22) Date of filing: **15.09.2014**

(51) Int Cl.:
B22F 1/00 ^(2006.01) **C22C 30/02** ^(2006.01)
C22C 30/06 ^(2006.01) **C22C 9/02** ^(2006.01)
C22C 1/04 ^(2006.01) **H01J 7/20** ^(2006.01)
H01J 9/395 ^(2006.01) **H01J 61/28** ^(2006.01)
H01J 7/18 ^(2006.01)

(86) International application number:
PCT/IB2014/064523

(87) International publication number:
WO 2015/052604 (16.04.2015 Gazette 2015/15)

(54) **A COMBINATION OF MATERIALS FOR MERCURY-DISPENSING DEVICES AND DEVICES
CONTAINING SAID COMBINATION OF MATERIALS**

KOMBINATION AUS MATERIALIEN FÜR QUECKSILBERAUSGABEVORRICHTUNGEN UND
VORRICHTUNGEN MIT DIESER KOMBINATION AUS MATERIALIEN

COMBINAISON DE MATÉRIAUX POUR DES DISPOSITIFS DE DISTRIBUTION DE MERCURE ET
DISPOSITIFS CONTENANT LADITE COMBINAISON DE MATÉRIAUX

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

(30) Priority: **08.10.2013 IT MI20131658**

(43) Date of publication of application:
22.07.2015 Bulletin 2015/30

(73) Proprietor: **Saes Getters S.p.A.
20020 Lainate (MI) (IT)**

(72) Inventors:
• **CORAZZA, Alessio**
I-22100 Como (CO) (IT)
• **DI GIAMPIETRO, Diego**
I-65122 Pescara (PE) (IT)

• **SANTELLA, Gianni**
I-67049 Tornimparte (AQ) (IT)

(74) Representative: **Concone, Emanuele et al**
Società Italiana Brevetti S.p.A.
Via Carducci 8
20123 Milano (IT)

(56) References cited:
EP-A1- 0 669 639 EP-A2- 0 737 995
US-A- 3 657 589

• **CORAZZA A ET AL: "Mercury dosing solutions
for fluorescent lamps", JOURNAL OF PHYSICS
D: APPLIED PHYSICS, INSTITUTE OF PHYSICS
PUBLISHING LTD, GB, vol. 41, no. 14, 21 July 2008
(2008-07-21) , page 144007, XP020133497, ISSN:
0022-3727**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to a combination of materials for the production of mercury-dispensing devices and to the mercury-dispensing devices thus produced.

[0002] The use of small amounts of mercury in lighting devices such as, for example, high pressure mercury discharge lamps, various kinds of alphanumeric displays, UV lamps and, particularly, fluorescent lamps is well known in the art.

[0003] An accurate and controlled dosage of mercury inside these devices is extremely important for the quality of the devices and most of all for environmental reasons. In fact, the high toxicity of this element implies serious problems of ecological nature upon end-life disposal of the devices containing it, or in case of accidental break-up of the devices.

These problems of ecological nature impose the use of amounts of mercury as small as possible, compatibly with the functionality of the tubes. These considerations have been lately included also in the legislative sphere, and the trend of the recent international regulations is to establish upper limits for the amount of mercury which can be introduced into the devices. For example, for standard fluorescent lamps the use of a total amount of Hg not greater than a few milligrams per lamp has been prescribed by the European RoHS Directive: less than 3 mg in linear Tri-band phosphor with normal lifetime and a tube diameter ≥ 9 mm and Tri-band phosphor with long lifetime (≥ 25.000 h); less than 3,5mg in linear Tri-band phosphor with normal lifetime and a tube diameter ≥ 17 mm; less than 5mg in linear Tri-band phosphor with long lifetime (≥ 25.000 h).

[0004] The old method of liquid mercury dosing first of all posed problems concerning not only the storing and handling of mercury in the plants for the production of tubes due to its high vapor pressure also at room temperature, but also the difficulty in precisely and reproducibly dosing volumes of mercury in the order of fractions of microliter.

[0005] These drawbacks led to the development of various techniques alternative to the use of liquid mercury in free form.

[0006] The use of liquid mercury contained in capsules, usually made of glass but possibly also metallic, is disclosed in several prior art documents as for example, respectively, in US 4823047 and US 4278908. After closing the lamp tube, the mercury is released within the lamp by means of a heat treatment which causes the breakage of the container. These methods generally have some drawbacks. First of all, the production of the capsules and their mounting inside the tubes may be complicated, especially when they have to be introduced inside small-size tubes. Secondly, the breakage of the capsule, particularly if it is made of glass, may produce fragments of material which can jeopardize the tube quality. Moreover, these systems still have the drawback of employing liquid mercury, and therefore they do not completely solve the problem of the precise and reproducible dosage of few milligrams of mercury.

[0007] These problems have been overcome by US patent no. 3657589 in the name of the applicant, which disclosed the use of intermetallic compounds of mercury having the general formula $Ti_xZr_yHg_z$, wherein x and y may vary between 0 and 13, the sum (x+y) may vary between 3 and 13 and z may be 1 or 2.

[0008] These compounds have a temperature of mercury-release start variable according to the specific compound, however they are all stable up to about 450°C both in the atmosphere and in evacuated volumes, thus resulting compatible with the operations for the assembly of the lighting devices, during which the mercury-dispensing devices may reach temperatures of about 400°C without risks of mercury loss. After closing the tube, the mercury is released from the above-cited compounds by an activation operation, which is usually carried out by heating the material at 900°C for about 30 seconds. This heating may be accomplished by laser radiation, or by induction heating of the dispenser device based on of the Hg-dispensing compound. The use of the Ti_3Hg compound is usually realized in the form of compressed powder in a ringshaped container or of compressed powder in pills or of a powder-coated metallic strip obtained by cold rolling.

[0009] These materials offer various advantages with respect to the prior art. As mentioned above, they avoid the risks of mercury evaporation during the cycle of production of the tubes, in which temperatures of about 350-400°C may be reached. Moreover, as described in the cited US 3657589, a getter material can be easily added to the mercury-dispensing compound with the purpose of chemisorption of gases such as CO, CO₂, O₂, H₂ and H₂O, which would interfere with the tube operation; the getter is activated during the same heat treatment for the release of mercury. Finally, the released amount of mercury is easily controllable and reproducible.

[0010] Despite their good chemi-physical characteristics and their great ease of use, these materials have the drawback that the contained mercury is not completely released during the activation treatment. This characteristic, together with the fact that the tube needs a certain amount of free mercury that is consumed during its life cycle, leads to the necessity of introducing into the device an amount of mercury which is about double than that which would theoretically be necessary.

[0011] In order to overcome these problems, the addition of Ni or Cu powders to the Ti_3Hg or Zr_3Hg compounds had been studied to favor the release of mercury. This solution is not completely satisfactory because, as it happens in the methods employing capsules, mercury bursts out violently and can cause damages to portions of the tube if the activation process is not precisely controlled; moreover the manufacturing of the container is quite complicated, since it requires the welding of small-size metallic members.

[0012] EP 0669639, in the applicant's name, discloses a mercury-dispensing intermetallic compound A including

mercury and a second metal selected among titanium, zirconium and mixtures thereof, and an alloy or an intermetallic copper-based compound B including tin, indium, silver or combinations thereof and possibly a third metal selected among the transition elements, wherein the transition metal is present in an amount not greater than 10% of the overall weight of component B.

[0013] Among the above-mentioned compositions A+B, those including Sn-Cu containing copper in the range between 3% and 63% on a weight basis are particularly preferred for the easy preparation and the good mechanical characteristics, and most of all the composition corresponding to the non-stoichiometric compound Cu_6Sn_5 .

[0014] A+B compositions that have been disclosed by EP 0669639, commonly named as high-yield Hg dispensing compositions, are characterized by the possibility to obtain, even at a relatively low temperature in the range 750-900°C, an effective Hg dispensation. In particular, those compositions are capable of releasing amounts of mercury higher than 60% during the activation step, even after partial oxidation, so as to be able to reduce the total amount of employed mercury. Drawbacks with these compositions are related to issues in the adherence of the powder mixture to the metallic container or support and in possible material detachment and flake-off with subsequent presence of loose particles in the lamp and reduction of the released mercury dose. Another drawback is that a partial premature mercury loss can occur from the EP 0669639 compositions in manufacturing processes with steps characterized by temperatures above 450°C, as for example in lamps productions carried out on high-temperature vertical lines.

[0015] An important advantage of the compositions according to the invention is related to the fact that the adhesion of the new mercury releasing powder mixture on the metallic holder or support is better than that of compounds known in the prior art, avoiding risks of powder loss or detachment from the support. This feature allows a more reliable handling and activation of the dispensing devices without problems of possible particles loss or material peel-off that can induce defects in the lamps or a reduction of the released mercury. A second technical advantage is that the premature mercury loss in the range 450°-550°C possibly achieved in high-temperature lamp production processes is significantly lower with respect to the EP 0669639 compositions, despite the fact that the activation temperature range is comparable.

[0016] Therefore, the object of the present invention is to provide an improved combination of materials for dispensing mercury in the lighting devices which allows to overcome one or more drawbacks of the prior art, in particular a combination allowing an effective Hg release only at temperatures greater than 750°C, and a mechanically stable dispenser structure which can be easily produced with commonly known metallurgical techniques.

[0017] According to the present invention, these and other objects are achieved by using a mercury-dispensing combination of materials made up of

- a mercury-dispensing compound A including mercury and a second metal selected among titanium, zirconium and mixtures thereof and
- an alloy or an intermetallic compound B including copper and tin, copper being present in an amount comprised between 35% and 90% weight percent with respect to the weight of said compound B,

characterized in that said mercury-dispensing combination of materials further contains an amount of oxygen comprised between 0,03% and 0,48% with respect to the overall weight of the composition A+B, preferably between 0,06% and 0,39% wt/wt. The above mentioned amounts of oxygen refer to an average content of O_2 in the A + B materials combination, measurable for example by means of an automatic gas analyzer on a suitable quantity of A+B mixture (at least 50 mg).

[0018] The alloy or intermetallic compound B could optionally further contain a third metal selected among the transition elements, with particular reference to iron, nickel, manganese and zinc wherein the transition metals are present in an amount not greater than 1% of the overall weight of compound B. In a preferred embodiment, the amount of transition metals does not exceed the amount corresponding to 0,5% weight percent of compound B. In another embodiment the amount of zinc or manganese in the alloy or intermetallic compound B does not exceed 0,3% weight percent of compound B or in a preferred embodiment 0,15% weight percent of compound B.

[0019] A mercury-dispensing device of the invention containing a combination of said materials A and B, can optionally further contain a getter material C, both mixed together with the materials A and B or present in a separate layer.

[0020] Further objects and advantages of the present invention will be apparent from the following detailed description referring to some not limiting embodiments.

[0021] Component A of the combination of the present invention, hereafter also defined mercury dispenser, is a compound containing one or more intermetallic materials corresponding to formula $\text{Ti}_x\text{Zr}_y\text{Hg}_z$, as disclosed in the cited US patent no. 3657589, to which reference is made for further details. Among the materials corresponding to said formula, Zr_3Hg and, particularly, Ti_3Hg are preferred.

[0022] Component B of the combination of the present invention has the function of favoring the release of mercury from component A, and hereafter will also be defined promoter. This component is an alloy or an intermetallic compound including copper and tin, copper being present in an amount comprised between 35% and 90% weight percent with respect to the weight of said compound B. It is also possible to use as component B alloys of three or more metals

obtained from the preceding ones by adding one or more elements selected among the transition metals in an amount not greater than 1% of the overall weight of component B. Preferably the transition metals are selected among iron, nickel, manganese and zinc. Preferably the amount of transition metals in the alloy or intermetallic compound B does not exceed the amount corresponding to 0,5% weight percent of compound B; in a more preferred embodiment the amounts of zinc or manganese are less than 0,3% weight percent of the total amount of compound B or even more preferably they do not exceed 0,15%.

[0023] The weight ratio between components A and B of the combination of the invention may vary within a wide range, but it is generally included between 10:1 and 1:10, and preferably between 7:1 and 1:5.

[0024] The best results are obtained when components A and B of the combination of the invention are in the form of a fine powder, having a particle size lower than 250 μm and preferably between 1 and 125 μm ; in more general terms it is intended that at least 95% of the employed particles have grain size features according to the above limits.

[0025] The present invention, in a second aspect thereof, relates to the mercury-dispensing devices which use the above-described combinations of A and B materials.

[0026] Some classes of lighting devices for which the mercury dispensers are intended further require, for their correct operation, the presence of a getter material C which removes traces of gases such as CO, CO₂, H₂, O₂ or water vapor: it is the case, for example, of fluorescent lamps that after the production process have a not negligible impurities level in the filling gas. For these applications, the getter can be advantageously introduced by means of the same mercury-dispensing device, according to the manners described in the cited US patent no. 3657589.

[0027] Examples of getter materials include, among the others, metals such as titanium, zirconium, tantalum, niobium, vanadium and mixtures thereof, or alloys thereof with other metals such as nickel, iron, aluminum, like the alloy having a weight percentage composition Zr 86%- Al 14%, or the intermetallic compounds Zr₂Fe and Zr₂Ni. The getter is activated during the same heat treatment by which mercury is released inside the tube.

[0028] The getter material C may be present in various physical forms, but it is preferably employed in the form of a fine powder, having a particle size lower than 250 μm and preferably between 1 and 125 μm .

[0029] The ratio between the overall weight of the A and B materials and that of the getter material C may generally range from about 10:1 to 1:10, and preferably between 5:1 and 1:2.

[0030] In a first possible embodiment, the devices of the invention can simply consist of a layer of powder mixture of the A and B (and optionally C) materials compressed on a metallic support or container which for ease of production generally has a cup shape or a ring shape. Supports acting as powders holders, such as those based on flat metallic surfaces, are particularly advantageous; such metallic supports are known in the technical field and represent an advantageous means to incorporate the mercury source within the fluorescent lamps. They are described, for example, in WO 97/019461 in the applicant's name and in US 5825127, whose teachings are herein incorporated by reference.

[0031] In the case of supported materials, the device may be made in the shape of a strip, preferably made of nickel-plated steel, onto which the A and B (and optionally C) materials are adhered by cold compression (rolling). In this case, whenever the presence of the getter material C is required, materials A, B and C may be mixed together and rolled on one or both faces of the strip but in a preferred embodiment materials A and B are placed on one surface of the strip and material C on the opposite surface.

[0032] In a second possible embodiment of the device according to the present invention the dispensing device has a ring-like configuration obtained by bending a metallic strip holding the A and B (and possibly C) materials and welding the strip overlapped extremities. Over the strip the A and B materials mixture is deposited and compressed in tracks and possibly separate tracks of a getter material can be present. Number and disposition of tracks and closing means for the support can vary without departing from the scope of the present invention.

[0033] One of the preferred ways to produce the support is to deposit the tracks by means of the cold rolling technique, i.e. by depositing tracks of the materials in powder form on a substrate and then by passing over a compressing roll. The support is then cut onto the desired length and given its final shape. The substrate is typically made of a metallic material: for example suitable materials are nickel-plated iron, nickel-iron alloys, stainless steel. With regards to the height of the tracks, it is advantageously less than 0,5 mm, the lowest limit given by the height of a particle monolayer.

[0034] Another advantageous variant for a device comprising the mercury dispensing composition to carry out the method according to the present invention consists of the metallic strip formed in a V shape by folding it approximately in the center; on the metallic strip is present at least a track of mercury releasing powders according to the present invention. In another variant the V shape support can host a track of mercury releasing powders and a track of getter alloy.

[0035] The method includes the step of introducing inside the tube the above-described mercury-dispensing combination of materials, preferably by means of one of the above-described devices, and then the combination heating step to release mercury. The heating step may be carried out with any suitable means such as, for example, by radiation, by high-frequency induction heating or by having a current flow through the support when the latter is made of a material having a high electric resistivity. The heating is applied at a temperature which causes the release of mercury from the mercury-dispensing combination, comprised between 700 and 900°C for a time of about 10 seconds to one minute.

[0036] The invention will be further illustrated by the following examples. These nonlimiting examples illustrate some

embodiments intended to teach to those skilled in the art how to put in practice the invention and to show the best mode to carry out the invention.

EXAMPLES

[0037] 100 grams of a mercury-dispensing mixture M1 are prepared according to the present invention by mixing 55 grams of a TiHg alloy powder containing 54% by weight of mercury and 45 grams of a CuSn alloy powder containing 85% by weight of copper and 15% by weight of Sn; the powder mixture has an average O₂ content of 0,333% wt;

[0038] 100 grams of a mercury-dispensing mixture M2, with the same composition of mixture M1, but with an average oxygen content of 0,076 %, are prepared according to the invention.

[0039] Also 100 grams of a mercury-dispensing mixture M3 are prepared according to the present invention by mixing 55 grams of a TiHg alloy powder containing 54% by weight of mercury and 45 grams of a CuSn alloy powder containing 41% by weight of copper and 59% by weight of tin; the powder mixture has an average O₂ content of 0,37% wt;

[0040] As comparative examples also 100g of mercury-dispensing mixtures C1 and C2 are prepared, with the same composition of M1 and M2 but with an average oxygen content of 0,027% wt and of 0,519% wt.

[0041] The five mixtures are used to prepare samples of powder-coated strips applying each powder mixture on a nickel-plated iron strip by cold rolling.

[0042] The five different coated strips are then evaluated in terms of Hg yield at 850°C for a total time of 30 seconds and in terms of adherence of the coating on the metallic substrate. In order to measure Hg yield, three samples of coated strip for each composition are tested. The samples are RF heated in a glass bulb under vacuum (pressure below 1*10⁻³ mbar) at 850°C for 20 seconds after a ramp-up time of 10 seconds: the measure of the sample weight difference after the applied heating process indicates the mercury release and, knowing the initial Hg content, the Hg yield is determined.

[0043] On other four samples for each composition the adherence of the powder mixture on the metallic strip is checked: a strip sample is bent around a metallic rod having a radius of 15 mm. Powder adherence is judged excellent when no flake-off or defects or cracks are observed on the coating after bending, adherence is good when just minor cracks without peel-off occur in limited areas of the samples (less than 7% of the total coating surface), adherence is not good when powder peel-off occurs or coating cracks are not localized in limited areas.

[0044] Data of average Hg yield obtained during activation at 850°C and results of the adherence tests are reported in the following table:

ID	Mixture Composition % wt	O ₂ content %wt	Hg Yield %	Adherence on strip
M1	TiHg + Cu85%Sn15%	0,333	96%	Excellent
M2	TiHg + Cu85%Sn15%	0,076	97%	Good
M3	TiHg + Cu41%Sn59%	0,370	96%	Good
C1	TiHg + Cu85%Sn15%	0,027	97%	Not good
C2	TiHg + Cu85%Sn15%	0,519	87%	Excellent

[0045] The samples show very good yields with the exception of C2 that has a low Hg yield; on the other hand C1 shows coating flake-off problems, whereby only the samples made according to the present invention show both high Hg yield and good/excellent powder adherence.

Claims

1. A mercury-dispensing combination of materials made up of

- a mercury-dispensing powder compound A including mercury and a second metal selected among titanium, zirconium and mixtures thereof and
- an alloy or an intermetallic powder compound B including copper and tin, copper being present in an amount comprised between 35% and 90% weight percent with respect to the weight of said compound B,

characterized in that said mercury-dispensing combination of materials further contains an amount of oxygen comprised between 0,03% and 0,48% with respect to the overall weight of the composition, preferably between 0,06% and 0,39% wt/wt.

2. A mercury-dispensing combination of materials according to claim 1, wherein the alloy or intermetallic compound B further contains at least a third metal selected among the transition metals iron, nickel, manganese and zinc and wherein the transition metals are present in an amount not greater than 1% of the overall weight of compound B.
- 5 3. A mercury-dispensing combination of materials according to claim 2, wherein the amount of transition metals does not exceed an amount corresponding to 0,5% weight percent of compound B.
4. A mercury-dispensing combination of materials according to claim 2 or 3, wherein the amount of zinc or manganese in the alloy or intermetallic compound B does not exceed 0,3% weight percent of compound B, preferably does not
10 exceed 0,15% weight percent of compound B.
5. A mercury-dispensing combination of materials according to any of the preceding claims, wherein the mercury-dispensing compound A is selected among compounds containing one or more intermetallic materials corresponding to formula $Ti_xZr_yHg_z$, preferably between the formulas Zr_3Hg and Ti_3Hg .
15
6. A mercury-dispensing combination of materials according to any of the preceding claims, wherein the weight ratio between components A and B of the combination is included between 10:1 and 1:10, preferably between 7:1 and 1:5.
7. A mercury-dispensing device containing a mercury-dispensing composition according to any of the preceding claims.
20
8. A mercury-dispensing device according to claim 7, wherein component B is present in the form of a coating of the metallic support, and component A as a powder adhered to component B by rolling.
9. A mercury-dispensing device according to claim 7, wherein components A and B are in the form of a fine powder
25 having a particle size lower than 250 μm , preferably between 1 and 125 μm .
10. A mercury-dispensing device according to any of claims 7 to 9, wherein at least a getter material C is added,
11. A mercury-dispensing device according to claim 10, wherein said getter material C includes metals such as titanium, zirconium, tantalum, niobium, vanadium and mixtures thereof or their alloys with other metals such as nickel, iron, aluminum, preferably the alloy having a weight percentage composition Zr 86%- 14% or the intermetallic compounds Zr_2Fe and Zr_2Ni .
30
12. A mercury-dispensing device according to claim 10 or 11, wherein the ratio between the overall weight of the A and B materials and the weight of the getter material C ranges from about 10:1 to 1:10, preferably between 5:1 and 1:2.
35
13. A mercury-dispensing device according to any of claims 7 to 12 wherein the mercury-dispensing composition adheres to a supporting material having the shape of a strip preferably made of nickel-plated steel.
14. A mercury-dispensing device according to claim 13, wherein materials A, B and C are mixed together and rolled on one or both faces of the strip.
40
15. A mercury-dispensing device according to claim 13, wherein materials A and B are placed on one surface of the strip and material C on the opposite surface with respect to materials A and B.
45

Patentansprüche

1. Eine Quecksilber freisetzende Kombination von Materialien, zusammengesetzt aus
50
 - einer Quecksilber freisetzenden Pulververbindung A, umfassend Quecksilber und ein zweites Metall, ausgewählt aus Titan, Zirkonium und Mischungen davon, und
 - einer Legierung oder einer intermetallischen Pulververbindung B, umfassend Kupfer und Zinn, wobei Kupfer in einer Menge zwischen 35% und 90% Gewichtsprozent, bezogen auf das Gewicht der Verbindung B, enthalten
55 ist,

dadurch gekennzeichnet, dass die Quecksilber freisetzende Kombination von Materialien ferner eine Sauerstoffmenge zwischen 0,03% und 0,48%, bezogen auf das Gesamtgewicht der Kombination, vorzugsweise zwischen

0,06% und 0,39% Gew./Gew. enthält.

2. Eine Quecksilber freisetzende Kombination von Materialien nach Anspruch 1, worin die Legierung oder intermetallische Verbindung B ferner mindestens ein drittes Metall enthält, ausgewählt aus den Übergangsmetallen Eisen, Nickel, Mangan und Zink, und wobei die Übergangsmetalle in einer Menge von nicht mehr als 1% des Gesamtgewichts der Verbindung B enthalten sind.
3. Eine Quecksilber freisetzende Kombination von Materialien nach Anspruch 2, worin die Menge an Übergangsmetallen eine Menge, die 0,5% Gewichtsprozent der Verbindung B entspricht, nicht übersteigt.
4. Eine Quecksilber freisetzende Kombination von Materialien nach Anspruch 2 oder 3, worin die Menge von Zink oder Mangan in der Legierung oder der intermetallischen Verbindung B 0,3% Gewichtsprozent der Verbindung B, vorzugsweise 0,15% Gewichtsprozent der Verbindung B nicht übersteigt.
5. Eine Quecksilber freisetzende Kombination von Materialien nach einem der vorhergehenden Ansprüche, worin die Quecksilber abgebende Verbindung A ausgewählt ist aus Verbindungen, die eine oder mehrere intermetallische Materialien enthalten, die der Formel $Ti_xZr_yHg_z$, vorzugsweise den Formeln Zr_3Hg und Ti_3Hg entsprechen.
6. Eine Quecksilber freisetzende Kombination von Materialien nach einem der vorhergehenden Ansprüche, worin das Gewichtsverhältnis zwischen den Komponenten A und B der Kombination zwischen 10:1 und 1: 10, vorzugsweise zwischen 7: 1 und 1: 5 liegt.
7. Eine Quecksilber freisetzende Vorrichtung, die eine Quecksilber freisetzende Zusammensetzung nach einem der vorhergehenden Ansprüche enthält.
8. Eine Quecksilber freisetzende Vorrichtung nach Anspruch 7, worin Komponente B in Form einer Beschichtung des metallischen Trägers vorliegt und Komponente A als Pulver durch Walzen an Komponente B angehaftet.
9. Eine Quecksilber freisetzende Vorrichtung nach Anspruch 7, worin die Komponenten A und B in der Form eines feinen Pulvers mit einer Teilchengröße von weniger als 250 μm , vorzugsweise zwischen 1 und 125 μm vorliegen.
10. Eine Quecksilber freisetzende Vorrichtung nach einem der Ansprüche 7 bis 9, worin zumindest ein Gettermaterial C hinzugefügt wurde.
11. Eine Quecksilber freisetzende Vorrichtung nach Anspruch 10, wobei das Gettermaterial C Metalle wie Titan, Zirkonium, Tantal, Niobium, Vanadium und deren Mischungen oder deren Legierungen mit anderen Metallen wie Nickel, Eisen, Aluminium enthält, wobei vorzugsweise die Legierung eine prozentuale Gewichts zusammensetzung von Zr 86% - Al 14% oder die intermetallischen Verbindungen Zr_2Fe und Zr_2Ni aufweist.
12. Eine Quecksilber freisetzende Vorrichtung nach Anspruch 10 oder 11, worin das Verhältnis zwischen dem Gesamtgewicht der Materialien A und B und dem Gewicht des Gettermaterials C im Bereich von etwa 10: 1 bis 1: 10, vorzugsweise zwischen 5: 1 und 1: 2 liegt.
13. Eine Quecksilber freisetzende Vorrichtung nach einem der Ansprüche 7 bis 12, worin die Quecksilber abgebende Zusammensetzung auf einem Trägermaterial in Form eines Streifens, der vorzugsweise aus vernickeltem Stahl hergestellt ist, haftet.
14. Eine Quecksilber freisetzende Vorrichtung nach Anspruch 13, worin die Materialien A, B und C miteinander vermischt und auf einer oder beiden Seiten des Streifens ausgerollt werden.
15. Eine Quecksilber freisetzende Vorrichtung nach Anspruch 13, worin die Materialien A und B auf einer Oberfläche des Streifens und das Material C auf der gegenüberliegenden Oberfläche in Bezug auf die Materialien A und B angeordnet sind.

Revendications

1. Combinaison de matériaux de distribution de mercure, constituée de :

- un composé pulvérulent de distribution de mercure A comprenant du mercure et un deuxième métal choisi parmi le titane, le zirconium et leurs mélanges et
- un alliage ou un composé pulvérulent intermétallique B comprenant du cuivre et de l'étain, le cuivre étant présent en une quantité comprise entre 35 % et 90 % en poids par rapport au poids dudit composé B,

caractérisée en ce que ladite combinaison de matériaux de distribution de mercure contient en outre une quantité d'oxygène comprise entre 0,03 % et 0,48 % par rapport au poids global de la composition, de préférence entre 0,06 % et 0,39 % en poids/poids.

2. Combinaison de matériaux de distribution de mercure selon la revendication 1, dans laquelle l'alliage ou le composé intermétallique B contient en outre au moins un troisième métal choisi parmi les métaux de transition fer, nickel, manganèse et zinc et dans laquelle les métaux de transition sont présents en une quantité qui n'est pas supérieure à 1 % du poids total du composé B.
3. Combinaison de matériaux de distribution de mercure selon la revendication 2, dans laquelle la quantité de métaux de transition n'excède pas une quantité correspondant à 0,5 % en poids du composé B.
4. Combinaison de matériaux de distribution de mercure selon la revendication 2 ou 3, dans laquelle la quantité de zinc ou de manganèse dans l'alliage ou le composé intermétallique B n'excède pas 0,3 % en poids du composé B, de préférence n'excède pas 0,15 % en poids du composé B.
5. Combinaison de matériaux de distribution de mercure selon l'une quelconque des revendications précédentes, dans laquelle le composé de distribution de mercure A est choisi parmi les composés contenant un ou plusieurs matériaux intermétalliques correspondant à la formule $Ti_xZr_yHg_z$, de préférence entre les formules Zr_3Hg et Ti_3Hg .
6. Combinaison de matériaux de distribution de mercure selon l'une quelconque des revendications précédentes, dans laquelle le rapport en poids entre les composants A et B de la combinaison est compris entre 10 :1 et 1 :10, de préférence entre 7 :1 et 1 :5.
7. Dispositif de distribution de mercure contenant une composition de distribution de mercure selon l'une quelconque des revendications précédentes.
8. Dispositif de distribution de mercure selon la revendication 7, dans lequel le composant B est présent sous la forme d'un revêtement du support métallique et le composant A sous la forme d'une poudre qui a adhéré au composant B par laminage.
9. Dispositif de distribution de mercure selon la revendication 7, dans lequel les composants A et B sont sous la forme d'une poudre fine ayant une taille de particules inférieure à 250 μm , de préférence comprise entre 1 et 125 μm .
10. Dispositif de distribution de mercure selon l'une quelconque des revendications 7 à 9, dans lequel au moins un matériau getter C est ajouté.
11. Dispositif de distribution de mercure selon la revendication 10, dans lequel ledit matériau getter C comprend des métaux tels que le titane, le zirconium, le tantale, le niobium, le vanadium, et des mélanges de ceux-ci ou leurs alliages avec d'autres métaux comme le nickel, le fer, l'aluminium, de préférence l'alliage ayant une composition en pourcentage en poids de Zr 86 % - Al 14 % ou les composés intermétalliques Zr_2Fe et Zr_2Ni .
12. Dispositif de distribution de mercure selon la revendication 10 ou 11, dans lequel le rapport entre le poids total des matériaux A et B et le poids des matériaux getter C va d'environ 10 :1 à 1 :10, est de préférence compris entre 5 :1 et 1 :2.
13. Dispositif de distribution de mercure selon l'une quelconque des revendications 7 à 12, dans lequel la composition de distribution de mercure adhère à un matériau de support ayant la forme d'une bande de préférence constituée d'un acier plaqué au nickel.
14. Dispositif de distribution de mercure selon la revendication 13, dans lequel les matériaux A, B et C sont mélangés ensemble et laminés sur une face ou les deux faces de la bande.

EP 2 895 287 B1

15. Dispositif de distribution de mercure selon la revendication 13, dans lequel les matériaux A et B sont placés sur une surface de la bande et le matériau C sur la surface opposée par rapport aux matériaux A et B.

5

10

15

20

25

30

35

40

45

50

55

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 4823047 A [0006]
- US 4278908 A [0006]
- US 3657589 A [0007] [0009] [0021] [0026]
- EP 0669639 A [0012] [0014] [0015]
- WO 97019461 A [0030]
- US 5825127 A [0030]

Szabadalmi igénypontok

1. Higanyt leadó anyagkeverék, amely
 - egy higanyt leadó poralakú A vegyületeiből, amely higanyt és egy, titán, cirkónium és ezek keverékei közül megválasztott második fémeket foglal magában, és
 - egy ötvözetből vagy egy B poralakú fémközi vegyületből, amely rézet és ónt foglal magában, ahol a réz mennyisége a B vegyület tömegére vonatkoztatva 35 tömeg% és 90 tömeg% közötti,
 áll, **azzal jellemezve, hogy a higanyt leadó anyagkeverék összítömegére vonatkoztatva járulékosan oxigént tartalmaz 0,03 tömeg % és 0,48 tömeg%, előnyösen 0,06 tömeg% és 0,39 tömeg% közötti mennyiségben.**
2. Az 1. igénypont szerinti higanyt leadó anyagkeverék, ahol az ötvözet vagy a B fémközi vegyület járulékosan legalább egy harmadik, vas, nikkel, mangán és cink átmeneti fémek közül megválasztott fémeket tartalmaz, és ahol az átmeneti fémek mennyisége a B vegyület összítömegére vonatkoztatva nem nagyobb, mint 1%.
3. Az 1. vagy 2. igénypont szerinti higanyt leadó anyagkeverék, ahol az átmeneti fémek mennyisége a B vegyületre vonatkoztatva nem nagyobb, mint 0,5 tömeg%.
4. A 2. vagy 3. igénypont szerinti higanyt leadó anyagkeverék, ahol az ötvözetben vagy a B fémközi vegyületben a cink vagy a mangán mennyisége a B vegyületre vonatkoztatva nem nagyobb, mint 0,3 tömeg%, előnyösen 0,15 tömeg%.
5. Az előző igénypontok bármelyike szerinti higanyt leadó anyagkeverék, ahol a higanyt leadó A vegyület egy vagy több, a $Ti_xZr_yHg_z$ képletnek megfelelő fémközi vegyület, előnyösen Zr_3Hg and Ti_3Hg képleteknek megfelelő vegyületek közül van megválasztva.
6. Az előző igénypontok bármelyike szerinti higanyt leadó anyagkeverék, ahol a keverék A és B komponensei közötti tömegarány 10:1 és 1:10, előnyösen 7:1 és 1:5 közötti.
7. Higanyt leadó berendezés, amely az előző igénypontok bármelyike szerinti higanyt leadó anyagkeveréket tartalmaz.
8. A 7. igénypont szerinti higanyt leadó berendezés, ahol a B komponens egy fémes hordozó bevonataként és az A komponens a B komponenshez hengerlés útján odatapasztott porként van jelen.
9. A 7. igénypont szerinti higanyt leadó berendezés, ahol az A és a B komponens 250 μm -nál kisebb, előnyösen 1 μm és 125 μm közötti szemeseméretű porként vannak jelen.
10. A 7 - 9. igénypontok bármelyike szerinti higanyt leadó berendezés, ahol legalább egy C getter anyag kerül adagolásra.
11. A 10. igénypont szerinti higanyt leadó berendezés, ahol a C getter anyag közé tartoznak fémek, például titán, cirkónium, tantál, nióbium, vanádium és ezek keverékei vagy ezek más fémekkel, például nikkellel, vassal vagy alumíniummal alkotott ötvözetek, előnyösen 86 % Zr-t és 14% Al-t tartalmazó ötvözet, vagy a Zr_2Fe és Zr_2Ni fémközi vegyületek.
12. A 10. vagy 11. igénypont szerinti higanyt leadó berendezés, ahol az A és B komponensek összítömege és a C getter anyag tömege közötti arány mintegy 10:1 és 1:10, előnyösen 5:1 és 1:2 közötti.
13. A 7 - 12. igénypontok bármelyike szerinti higanyt leadó berendezés, ahol a higanyt leadó keverék csík alakú, előnyösen nikkellel bevont acélból készült hordozóhoz tapad.

14. A 13. igénypont szerinti higanyt leadó berendezés, ahol az A, B és C anyagok össze vannak keverve és a csík egyik vagy mindkét oldalára vannak hengerelve.

15. A 13. igénypont szerinti higanyt leadó berendezés, ahol az A és B anyagok a csík egyik oldalán és a C anyag a csíknak az A és B anyagok vonatkozásában ellentétes oldalán vannak elhelyezve.