(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 815 821 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
24.12.2014 Bulletin 2014/52

(21) Application number: **13305813.1**

(22) Date of filing: **17.06.2013**

(51) Int Cl.:
B22F 1/00 *(2006.01)* ***B22F 9/06*** *(2006.01)*
B01J 19/28 *(2006.01)* ***B03B 5/32*** *(2006.01)*
B04B 1/00 *(2006.01)*

(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
Designated Extension States:
BA ME

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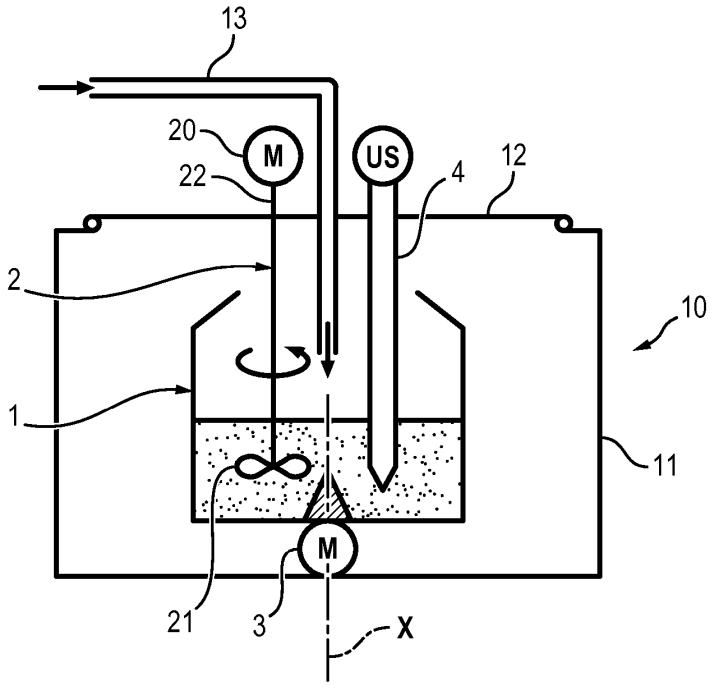
(54) Process and device for cleaning metal containing particles forming a powder by removing a compound attached to the particles

(57) The invention relates to a process for cleaning metal-containing particles, said particles forming a powder, by removing a compound attached to the particles, comprising the following steps:
(a) providing a container (1),
(b) providing in said container (1) a composition comprising particles suspended in a solvent of said compound,
(c) centrifuging the composition in said container (1) to provide a sediment phase (S) and a fluid phase (F),
(d) during or after centrifuging step (c), removing at least a part of said fluid phase (F),
(e) supplying a further portion of solvent to the sediment phase (S) in said container (1),
(f) stirring the composition so as to suspend the particles in the solvent,
(g) repeating steps (c) and (d).

The invention also relates to a device for carrying out such a process.

FIG. 1



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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a process and a device for cleaning metal-containing particles forming a powder by removing a compound attached to the particles.

[0002] The invention can in particular be applied for cleaning metal-containing particles contaminated by oil.

BACKGROUND OF THE INVENTION

[0003] Miniaturization in electronic field request finer solder pitch, which can only be achieved using finer solder powder.

[0004] This invention relates to the production means of these ultrafine solder powders.

[0005] The term "powder" herein designates here particles having an average diameter of less than 25 μm.

[0006] Ultrafine solder powder is produced by dispersing melted metal-containing alloy in a dispersing media.

[0007] For example, an ingot made of said alloy is provided in a fluid compound.

[0008] Said ingot is heated to a temperature above the melting temperature of the alloy.

[0009] A mixture of two fluid phases is thus created: a first fluid phase consisting of the fluid compound and the second fluid phase consisting of the melted alloy.

[0010] Said mixture is then subjected to shearing strain so as to create an emulsion of melted alloy droplets in the fluid compound.

[0011] The droplets are then solidified so as to form metal-containing particles that may be used as a solder powder.

[0012] An example of such a method is described in document WO 00/00313.

[0013] Oil is a medium usually used to melt metal or alloy and get high dispersion performance.

[0014] However, a significant drawback of this manufacturing process is the necessity to clean the powder after dispersion, in order to remove oil attached to the particles of the powder.

[0015] Indeed, in microelectronics, the powder is intended to be mixed with a flux so as to form a solder cream, which is deposited on circuit boards so as to form solder bumps in order to connect electronic components.

[0016] The cleanliness of the powder is an issue since the presence of a contamination such as oil is likely to deteriorate the quality of the electrical connection.

[0017] A continuous cleaning process, involving the circulation of the particles within a solvent flow and the retention of the cleaned particles by a filter cannot be carried out to clean such a fine powder.

[0018] Indeed, this continuous cleaning process would imply using a filter having very small pores to be able to retain the particles; however, such a filter would create very high pressure loss, which would render the cleaning process unpractical.

[0019] Conversely, if a larger filter was used, it would not be able to retain the particles.

[0020] In addition, since the powder is very dense, it can hardly be rendered fluid enough to be compatible with a solvent flow.

[0021] Document EP 1 396 551 describes a device for cleaning oil-adhered particles that comprises an agitation tank and a centrifugal apparatus coupled to the agitation tank by a conveying apparatus.

[0022] The particles are first agitated with a solvent in the agitation tank, then transferred, via the conveying apparatus, to the centrifugal apparatus where the mixture is centrifuged.

[0023] The centrifugal apparatus includes a central screw intended to separate the particles from the solvent, the particles being directed downwards while the solvent and oil are directed upwards.

[0024] Due to the presence of the central screw, the centrifugal apparatus is difficult and tedious to clean.

[0025] In addition, if an additional cleaning is to be carried out, the particles have to be transferred to the agitation tank in order to be mixed with fresh solvent and then conveyed again to the centrifugal apparatus for the centrifugation step.

[0026] All these transfer steps require specific conveying means that render the cleaning device complex and that increase the duration of the cleaning process.

[0027] Another issue with the cleaning of the contaminated particles is that solvent is harmful for the human operators and for the environment.

[0028] It is thus desirable to minimize the amount of solvent needed to clean the particles. Besides, the cleaning step should be compatible with an industrial process.

[0029] It is thus desirable to have a cleaning process that may be automatized and that minimizes manpower resources.

[0030] Such process should also be as short as possible and allow treating large amounts of particles at the same time.

[0031] Such process should also minimize safety and environmental hazard.

[0032] A goal of the invention is also to provide a device for carrying out such a process.

[0033] Said device should allow a shorter cleaning and an easier maintenance (especially washing) that known devices.

[0034] Said device should also allow repeating the cleaning steps in a simple way, as long as the desired cleanliness has not been obtained.

[0035] Such device should be of dimensions compatible with an industrial process and should be operated using minimal manpower.

BRIEF DESCRIPTION OF THE INVENTION

[0036] An object of the invention is a process for cleaning metal-containing particles, said particles forming a

powder, by removing a compound attached to the particles, comprising the following steps:

(a) providing a container,
(b) providing in said container (1) a composition comprising said particles with the compound attached thereon and a solvent of said compound, the particles being suspended in said solvent,
(c) centrifuging the composition in said container (1) to provide a sediment phase (S) comprising said particles and a fluid phase (F) comprising said solvent and said compound,
(d) during or after centrifuging step (c), removing at least a part of said fluid phase (F) from the container (1),
(e) supplying a further portion of solvent to the sediment phase (S) in said container (1),
(f) stirring the composition comprising the sediment phase and the solvent in the container (1) so as to suspend the particles in the solvent,
(g) repeating steps (c) and (d).

[0037] By "metal-containing particle" is meant here a particle that comprises at least one metal; such a particle may be formed of an alloy of two or more metals.

[0038] According to a preferred embodiment, the metal-containing particle is made of a solder alloy usable in microelectronics.

[0039] Step (b) may comprise stirring the composition in the container before centrifuging step (c).

[0040] Advantageously, ultrasonic treatment of the composition is carried out during stirring.

[0041] Optionally, during stirring step (c) the container is rotated at a rotational speed that is less than the rotational speed of centrifugation step (d).

[0042] The process may further comprise repeating steps (e) to (g) at least once.

[0043] According to an embodiment, the process comprises, after the last fluid phase removal step, the further steps of:

(h) supplying a further portion of the solvent to the sediment phase in the container and stirring said portion of the solvent with the sediment phase so as to suspend the particles in the solvent,
(i) allowing said mixture to stand until sedimentation of said particles has occurred, thereby providing a sediment phase and a fluid phase, and
(j) removing the fluid phase.

[0044] After step (h) the stirred composition may be transferred into a column-shaped container and steps (i) and (j) are carried out in said column-shaped container.

[0045] After the transfer of the composition in the column-shaped container, a further stirring of said composition is advantageously performed before sedimentation step (i).

[0046] An ultrasonic treatment may be carried out during said further stirring step.

[0047] The average size of the particles is preferably less than 25 micrometer.

[0048] A further object of the invention is a device for carrying out such a process.

[0049] Said device comprises:

- a container for receiving a composition comprising said particles with the compound attached thereon and a solvent of said compound, said container being adapted to be subjected to rotation,
- at least one stirrer arranged at least partially into the container so as to stir said composition and suspend the particles in the solvent,
- a centrifuge arranged to rotate the container at a speed suitable for centrifuging the composition.

[0050] According to an advantageous embodiment, said device further comprises an ultrasonic vibrator extending at least partially into the container.

[0051] Said device may further comprise a column-shaped container coupled to the rotatable container by a conveying pipe adapted to transfer a composition comprising the solvent and the particles suspended in said solvent from the rotatable container to the column-shaped container.

[0052] A further object of the invention is a process of manufacturing a powder made of metal-containing particles.

[0053] Said process comprises:

- providing an ingot made of said metal in a fluid compound,
- heating the ingot to a temperature above the melting temperature of the metal so as to create a mixture of two fluid phases, a first fluid phase consisting of the fluid compound and the second fluid phase consisting of the melted metal,
- subjecting said mixture to shearing strain so as to create an emulsion of melted metal droplets in the fluid compound,
- solidifying the metal droplets so as to form said metal-containing particles,
- cleaning the metal-containing particles by carrying out a cleaning process as described above.

[0054] According to a preferred embodiment, the fluid compound comprises oil.

BRIEF DESCRIPTION OF THE DRAWINGS

[0055] Further features, embodiments and advantages of the invention will be apparent from the following detailed description, referring to the appended drawings wherein:

- Figure 1 schematically illustrates a cleaning device according to an embodiment of the invention, imple-

mented for stirring a composition comprising the particles to be cleaned and a solvent,

- Figure 2 schematically illustrates the cleaning device of figure 1, implemented to carry out centrifugation of the composition,
- Figure 3 schematically illustrates a separation device forming part of the cleaning device according to an embodiment of the invention.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0056] The particles to be cleaned are provided with a compound attached thereto.

[0057] Although this is not intended to be limitative, this compound may have been attached during the manufacturing process of the particles.

[0058] For example, if the particles have been produced by the dispersion of an alloy in a fluid medium, the compound comprises said medium.

[0059] The compound may consist of a single component or of a mixture of different components.

[0060] Examples of compounds that may be attached to the metal-containing particles comprise: residues of organic oils (e.g. synthetic oil, polyolefin oil, vegetable oil such as castor oil), residues of mineral oils (e.g. silicone oil), organic acids, polymer resins, amines, organometallic compounds, metal oxides.

[0061] In the embodiments described here, the compound to be removed from the particles is typically oil.

[0062] However, the skilled person is able to determine a suitable solvent for a given compound and could thus carry out the process described below to remove another kind of compound than oil without departing from the scope of the invention.

[0063] By "solvent" is meant herein a fluid wherein a given amount of the compound to be removed from the metal-containing particles can be dissolved at room temperature (25°C).

[0064] According to a preferred embodiment, the solubility of the compound in the solvent at room temperature is at least 10 g/l, i.e. it is possible to dissolve at least 10 g of the compound in 1 l of solvent.

[0065] Depending on the compound to remove, examples of solvents that may be used in the invention comprise: organic solvents such as non-polar solvents (e.g. pentane, hexane, cyclohexane, benzene, toluene, xylene) or polar solvents (e.g. dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetone, isopropanol), halogenated solvents (e.g. trichloroethane, tetrachloroethane, dichloromethane), water with surface active agent.

[0066] For example, acetone, isopropanol and halogenated solvents can be used as a solvent for castor oil residues.

[0067] A device for carrying out at least the first steps of the cleaning process is shown in Figure 1.

[0068] Said device comprises a container 1 that is intended to receive a composition comprising the particles to be cleaned and a solvent for the compound to be removed.

[0069] The container has a general symmetry of revolution around a vertical axis X.

[0070] For example, the container 1 has a bowl shape.

[0071] In the present text, "horizontal" refers to the plane of the ground of the installation where the cleaning device is installed, "vertical" referring to the direction orthogonal to said horizontal plane.

[0072] The container 1 is adapted to be subjected to rotation around its vertical axis, from low rotational speed up to speed suitable for centrifugation of the composition.

[0073] To that end, the container 1 is coupled to a centrifuge 3, in a way that is known per se.

[0074] Since the solvent used to clean the particles may be hazardous for the human operators and/or for the environment, the container 1 is advantageously placed in an enclosure that is closed hermetically.

[0075] In the embodiment illustrated here, the enclosure 10 comprises at least vertical walls 11 surrounding the container, and a cover 12 on top of the walls 11 and allowing access to the container 1, e.g. for maintenance or washing purposes.

[0076] The cover 12 may advantageously be crossed by a feed pipe 13 that is intended to introduce solvent (if the particles are already in the container) or a suspension comprising particles to be cleaned and solvent into the container.

[0077] Advantageously, the cover 12 may also be employed as a support for devices that may be used to clean the particles.

[0078] In particular, the device further comprises at least one stirrer 2 arranged at least partially into the container 1 so as to stir said composition.

[0079] The stirrer typically comprises a motor 20 that is arranged outside of the cover and a stirring component 21 linked to the motor 20 by a rod 22.

[0080] The stirrer is known per se and will not be described in more detail.

[0081] The stirrer 2 may be supported by the cover 12.

[0082] For example, as schematically illustrated in Figure 1, the motor 20 may be arranged above the cover 12 while the rod 22 crosses the cover 12, such that the stirring component 21 is immersed in the composition.

[0083] In use, the metal-containing particles to be cleaned are put in the container 1, the solvent is put into the container 1 by the feed pipe 13, and the composition is stirred by the stirrer 2.

[0084] This stirring step has the effect of suspending the particles in the solvent and also of making the compound be at least partially released from the particles and pass into the solvent, thereby washing at least partially the particles.

[0085] Optionally, the stirring may be assisted by an ultrasonic treatment that improves the efficiency in removing the compound from the particles.

[0086] To that end, an ultrasonic vibrator 4 is at least

partially immersed in the composition during operation of the stirrer 2.

[0087] For example, the ultrasonic vibrator 4 may be supported by the cover 12.

[0088] Optionally, during the stirring step, the container may be rotated at a low speed, i.e. a speed that is less than the centrifuging speed, e.g. between 20 and 200 rpm.

[0089] This rotation at low speed allows homogeneous washing by subjecting the whole powder to the stirrer effect.

[0090] The stirring step can be omitted if a suspension of the particles within the solvent is directly introduced in the container 1.

[0091] Once the particles are suspended within the solvent in the container, a first centrifuging step is carried out.

[0092] To that end, the cover 12 supporting the stirrer 2, the feed pipe 13 and optionally the ultrasonic vibrator 4 is removed and replaced by a cover 12' supporting a take-off pipe 13', as shown in Figure 2.

[0093] The container 1 is then rotated at high speed by the centrifuge 3. For example, the acceleration is between 300 and 3000 g.

[0094] As a result of this centrifugation, the composition is dissociated into two phases:

- a sediment phase consisting of the particles from which the compound has been at least partially removed, and
- a fluid phase containing the solvent and the compound removed from the particles.

[0095] The sediment phase S accumulates on the walls of the container 1, whereas the fluid phase F is at least partially extracted by the take-off pipe 13'.

[0096] The removal of the fluid phase may be carried out during and/or after the centrifugation step.

[0097] The sequence consisting of stirring and centrifuging the composition is carried out at least twice to improve the cleaning of the particles.

[0098] To that end, after the above-described first centrifuging step, fresh solvent is added into the container and the composition is first stirred (optionally assisted by the ultrasonic treatment) and then centrifuged again.

[0099] In the case where a device as illustrated in Figures 1 and 2 is used, this additional sequence supposes to remove the cover 12' and place again the cover 12 to close the enclosure 10, supply the fresh solvent via the feed pipe 13, actuate the stirrer 2 and, if appropriate, the ultrasonic vibrator 4.

[0100] Of course, the container 1 may also be rotated at a low speed during this stirring step.

[0101] Then, when the composition has been sufficiently stirred, the cover 12 is removed and replaced by the cover 12', and the container 1 is rotated at the centrifugation speed so as to provide a sediment phase comprising the particles and a fluid phase comprising the solvent and the compound.

[0102] Hence, the stirring steps are carried out in the same container than the centrifuging steps, which avoids conveying the mixture of the particles and the solvent between different devices to carry out the cleaning.

[0103] This sequence of stirring and centrifuging steps may be implemented as many times as necessary.

[0104] Different alternatives may be considered for the completion of the cleaning process.

[0105] According to a first alternative, at least part of the fluid phase is removed from the container 1 and the sediment phase consisting of the cleaned particles can be retrieved.

[0106] Then, the particles are dried and packed.

[0107] According to a second alternative, the particles have to be suspended again in a solvent in view of subsequent treatments, e.g. in view in their transfer to another device wherein the cleaning process will be completed.

[0108] After the last centrifugation step and removal of at least a part of the fluid phase, fresh solvent is supplied again in the container 1 and stirring of the composition is carried out so as to suspend the particles in the solvent.

[0109] After being stirred, the mixture consisting of the solvent and the suspended particles can be transferred to a column-shape container 5.

[0110] As shown on Figure 3, said container 5 has the general form of a column, i.e. it has an elongated shape extending vertically; for example, the column is a cylinder having a vertical revolution axis.

[0111] The container 5 may be made of glass. It can thus be easily cleaned and one can easily observe the sedimentation step and determine when sedimentation is completed.

[0112] The column-shaped container 5 is closed at both ends.

[0113] The upper end is closed by a cover 51.

[0114] This cover 51 is crossed by a stirrer 6, a feed pipe 52 for the mixture of the particles and the solvent transferred from the container 1, a feed pipe 53 for fresh solvent, a take-off pipe 54 to remove used solvent for the container 5 and optionally by an ultrasonic vibrator 7.

[0115] The feed pipe 52 is advantageously coupled to the container 1 by a conveying pipe (not shown) so as to transfer directly the particles in suspension in the solvent from the container 1 to the container 5.

[0116] The bottom end of the container 5 comprises a collection valve 50.

[0117] During cleaning of the particles, the collection valve 50 is closed.

[0118] The collection valve 50 is opened when the cleaning is finished, in order to release the cleaned particles from the column-shaped container 5.

[0119] In this column-shaped container 5, the mixture is again stirred by the stirrer 6 and, optionally, by the ultrasonic vibrator 7.

[0120] Then, the stirrer 6 is raised out of the mixture and the mixture is allowed to stand in the container 5 until

sedimentation of the particles has occurred.

[0121] The sediment phase is thus on the bottom of the column-shaped container 5, the fluid phase being above the sediment phase.

[0122] The take-off pipe 54 is then lowered down until the sediment phase-fluid phase interface, and the fluid phase is pumped.

[0123] Then, fresh solvent is fed by the feed pipe 53 and the particles are suspended in this fresh solvent by the stirrer 6 and, if appropriate, the ultrasonic vibrator 7.

[0124] If it is considered that the cleaning has been completed, the collection valve 50 is opened and the clean particles within the solvent are collected.

[0125] Otherwise, if additional cleaning steps are required, the mixture is allowed to stand until sedimentation occurs and the subsequent steps are repeated.

[0126] Since the particles have been at least partially cleaned by the stirring-centrifugation sequence(s) in the container 1, the last cleaning step carried out in the column-shaped container 5 is quicker since there remains only a little amount of compound attached to the particles.

[0127] As a consequence, said last cleaning step can be carried out in a few hours, whereas it would take several days if the initial amount of the compound was attached to the particles.

[0128] Another advantage of transferring the cleaned particles in the column-shaped container 5 to complete the cleaning is that this second container is cleaner that the first container 1.

[0129] Hence, it allows obtaining a greater final cleanliness of the particles.

[0130] Finally the treatment in the column-shaped container allows a separation of the particles according to their mass: during the stirring or the beginning of the sedimentation, coarser particle quickly fall on the bottom of the column, whereas lighter particles stay on the top a longer time. It is thus possible to pump out the lighter (finer) or the heavier (coarser) particles to reach the requested particles size distribution.

[0131] After cleaning, the particles are dried and packed.

[0132] The above-described cleaning process may advantageously be carried out after a manufacturing process of a powder formed of metal-containing particles, comprising:

- providing an ingot made of said metal in a fluid compound,
- heating the ingot to a temperature above the melting temperature of the metal so as to create a mixture of two fluid phases, a first fluid phase consisting of the fluid compound and the second fluid phase consisting of the melted metal,
- subjecting said mixture to shearing strain so as to create an emulsion of melted metal droplets in the fluid compound,
- solidifying the metal droplets so as to form said metal-containing particles.

[0133] One can refer to document WO 00/00313 for more details about said manufacturing process.

Claims

1. Process for cleaning metal-containing particles, said particles forming a powder, by removing a compound attached to the particles, comprising the following steps:

   (a) providing a container (1),
   (b) providing in said container (1) a composition comprising said particles with the compound attached thereon and a solvent of said compound, the particles being suspended in said solvent,
   (c) centrifuging the composition in said container (1) to provide a sediment phase (S) comprising said particles and a fluid phase (F) comprising said solvent and said compound,
   (d) during or after centrifuging step (c), removing at least a part of said fluid phase (F) from the container (1),
   (e) supplying a further portion of solvent to the sediment phase (S) in said container (1),
   (f) stirring the composition comprising the sediment phase and the solvent in the container (1) so as to suspend the particles in the solvent,
   (g) repeating steps (c) and (d).

2. Process according to claim 1, **characterized in that** step (b) comprises stirring the composition in the container (1) before centrifuging step (c).

3. Process according to claim 1 or claim 2, **characterized in that** ultrasonic treatment of the composition is carried out during stirring.

4. Process according to one of claims 1 to 3, **characterized in that** it comprises repeating steps (e) to (g) at least once.

5. Process according to one of claims 1 to 4, **characterized in that** it comprises, after the last fluid phase removal step, the further steps of:

   (h) supplying a further portion of the solvent to the sediment phase (S) in the container (1) and stirring said portion of the solvent with the sediment phase so as to suspend the particles in the solvent,
   (i) allowing said mixture to stand until sedimentation of said particles has occurred, thereby providing a sediment phase (S) and a fluid phase (F), and
   (j) removing the fluid phase (F).

6. Process according to claim 5, **characterized in that**

after step (h) the stirred composition is transferred into a column-shaped container (5) and **in that** steps (i) and (j) are carried out in said column-shaped container (5).

7. Process according to claim 6, **characterized in that** after the transfer of the composition in the column-shaped container (5) a further stirring of said composition is performed before sedimentation step (i).

8. Process according to claim 7, **characterized in that** an ultrasonic treatment is carried out during said further stirring step (h).

9. Process according to one of claims 1 to 8, **characterized in that** the average size of the particles is less than 25 micrometer.

10. Process of manufacturing a powder formed of metal-containing particles, comprising:

- providing an ingot made of said metal in a fluid compound,
- heating the ingot to a temperature above the melting temperature of the metal so as to create a mixture of two fluid phases, a first fluid phase consisting of the fluid compound and the second fluid phase consisting of the melted metal,
- subjecting said mixture to shearing strain so as to create an emulsion of melted metal droplets in the fluid compound,
- solidifying the metal droplets so as to form said metal-containing particles,
- cleaning the metal-containing particles by carrying out a cleaning process according to one of claims 1 to 9.

11. Process according to claim 10, wherein the fluid compound is oil.

12. Device for cleaning metal-containing particles forming a powder by removing a compound attached to the particles, comprising:

- a container (1) for receiving a composition comprising said particles with the compound attached thereon and a solvent of said compound, said container (1) being adapted to be subjected to rotation,
- at least one stirrer (2) arranged at least partially into the container (1) so as to stir said composition and suspend the particles in the solvent,
- a centrifuge (3) arranged to rotate the container (1) at a speed suitable for centrifuging the composition.

13. Device according to claim 12, **characterized in that** it further comprises an ultrasonic vibrator (4) extending at least partially into the container (1).

14. Device according to one of claims 12 or 13, **characterized in that** it further comprises a column-shaped container (5) coupled to the rotatable container (1) by a conveying pipe adapted to transfer a composition comprising the solvent and the particles suspended in said solvent from the rotatable container (1) to the column-shaped container (5).

FIG. 1

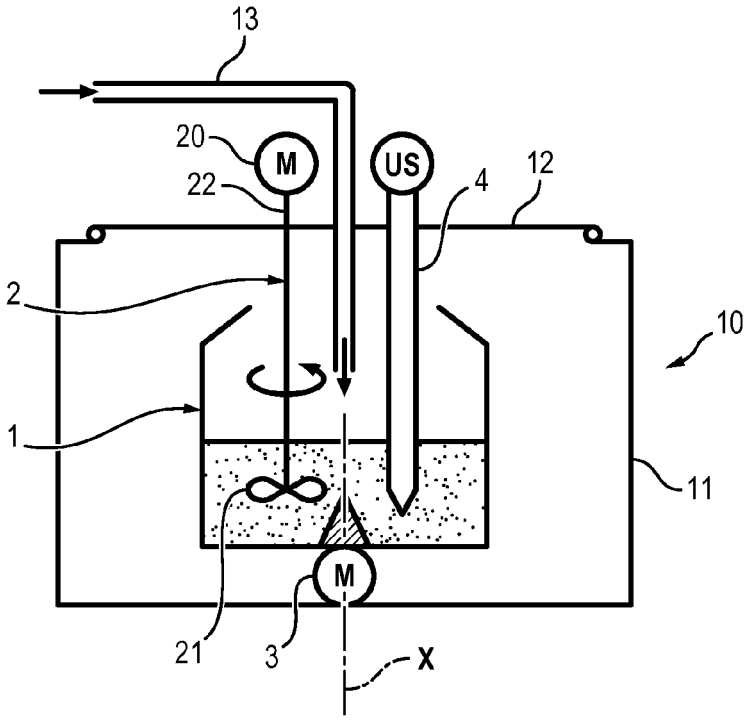


FIG. 2

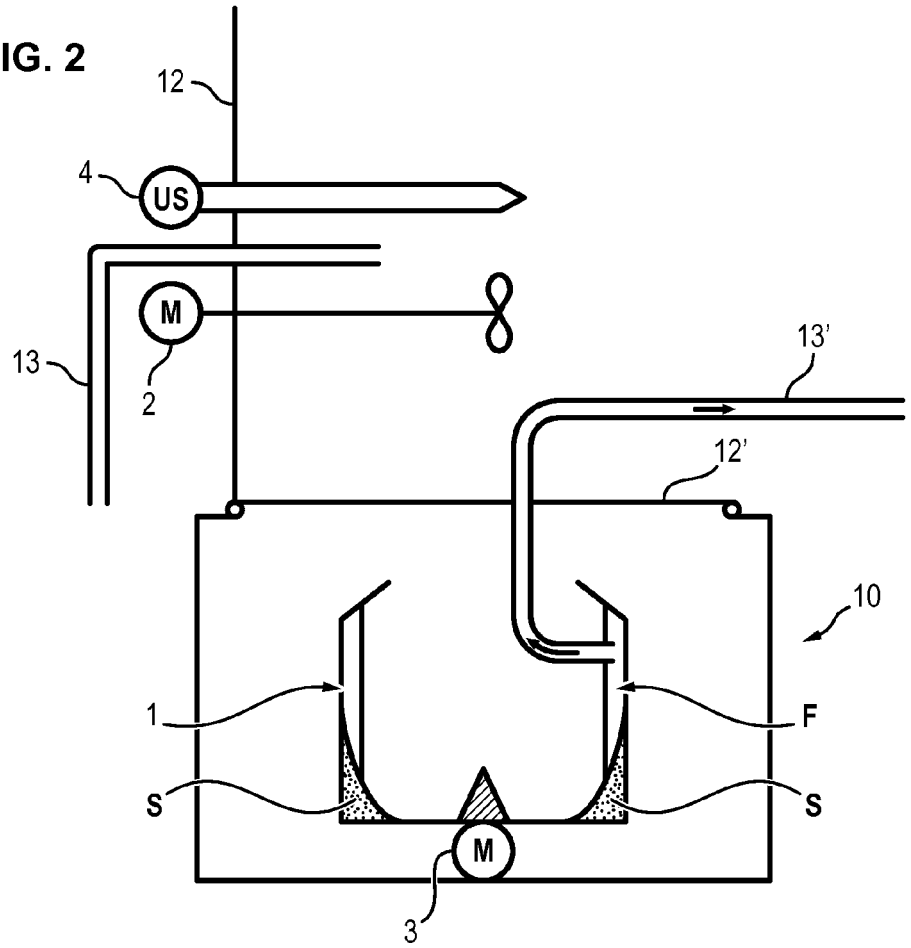
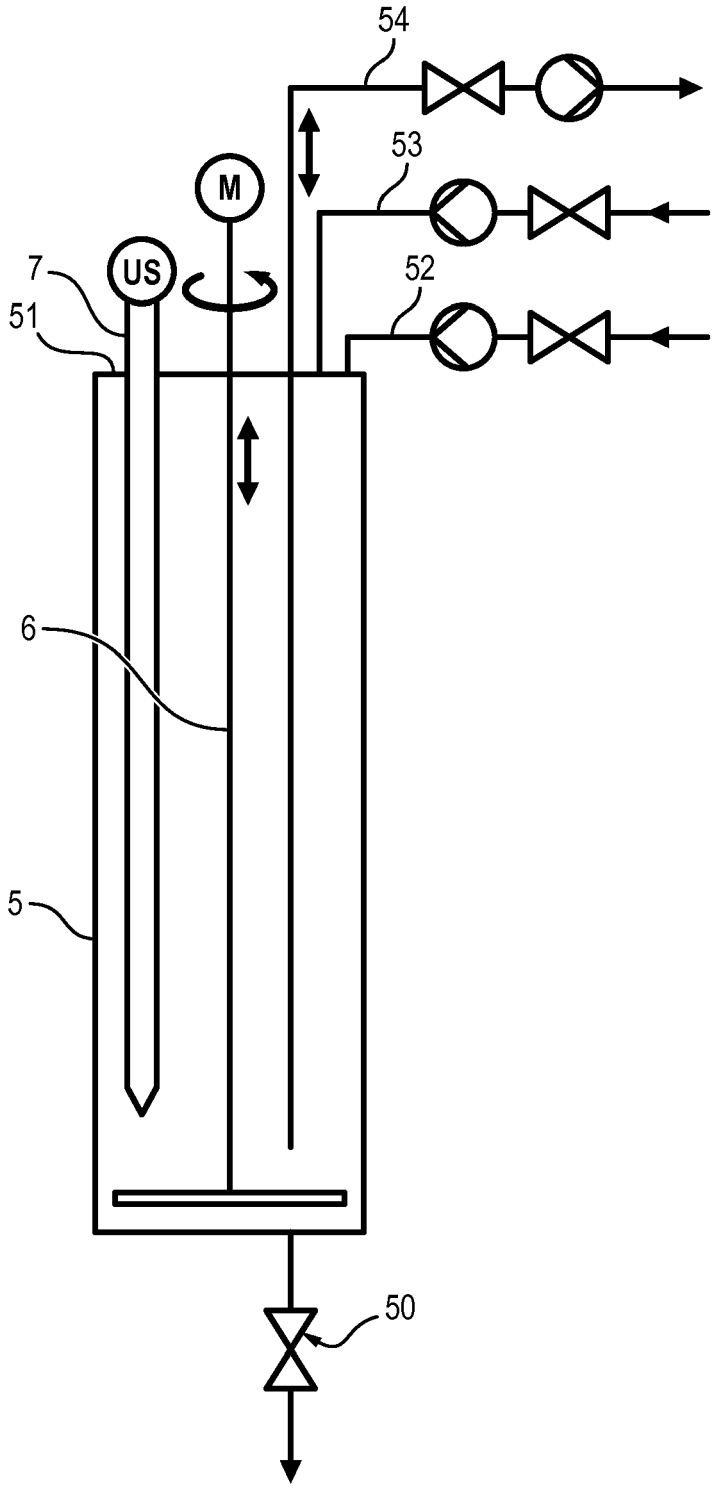


FIG. 3



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EUROPEAN SEARCH REPORT

Application Number
EP 13 30 5813

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2003/177865 A1 (ONO TAKAO [JP] ET AL) 25 September 2003 (2003-09-25) * paragraph [0002] * * paragraph [0013] * * paragraph [0022] - paragraph [0029] * * paragraph [0032] - paragraph [0033] * * paragraph [0116] - paragraph [0118] * * paragraph [0127] - paragraph [0129] * * claims; figures; examples *	1,2,4,5, 9-13	INV. B22F1/00 B22F9/06 B01J19/28 B03B5/32 B04B1/00
X	DE 40 19 232 A1 (AKAD WISSENSCHAFTEN DDR [DE]) 19 December 1991 (1991-12-19) * column 1, line 3 - line 12 * * column 2, line 16 - line 44 * * column 3, line 9 - line 40 * * claims; example *	1,4	
X	US 7 608 461 B1 (SIMMONS BLAKE A [US] ET AL) 27 October 2009 (2009-10-27) * column 5, line 1 - line 6 * * column 5, line 62 - column 6, line 11 * * claims 1,5 *	1,4,9	
A	WO 92/22620 A1 (RIG TECHNOLOGY LTD [GB]) 23 December 1992 (1992-12-23) * the whole document *	1,13	TECHNICAL FIELDS SEARCHED (IPC) B22F B01J B01F B03B B04B
A	WO 93/02221 A2 (MINNESOTA MINING & MFG [US]) 4 February 1993 (1993-02-04) * the whole document *	1-11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	12 November 2013	Ceulemans, Judy

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 13 30 5813

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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12-11-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003177865 A1	25-09-2003	JP 2003268418 A	25-09-2003
		US 2003177865 A1	25-09-2003
DE 4019232 A1	19-12-1991	NONE	
US 7608461 B1	27-10-2009	NONE	
WO 9222620 A1	23-12-1992	AU 1899392 A	12-01-1993
		DE 69214449 D1	14-11-1996
		DE 69214449 T2	20-02-1997
		EP 0588865 A1	30-03-1994
		WO 9222620 A1	23-12-1992
WO 9302221 A2	04-02-1993	JP H0533017 A	09-02-1993
		WO 9302221 A2	04-02-1993

EPO FORM P0459

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 0000313 A **[0012] [0133]**
- EP 1396551 A **[0021]**