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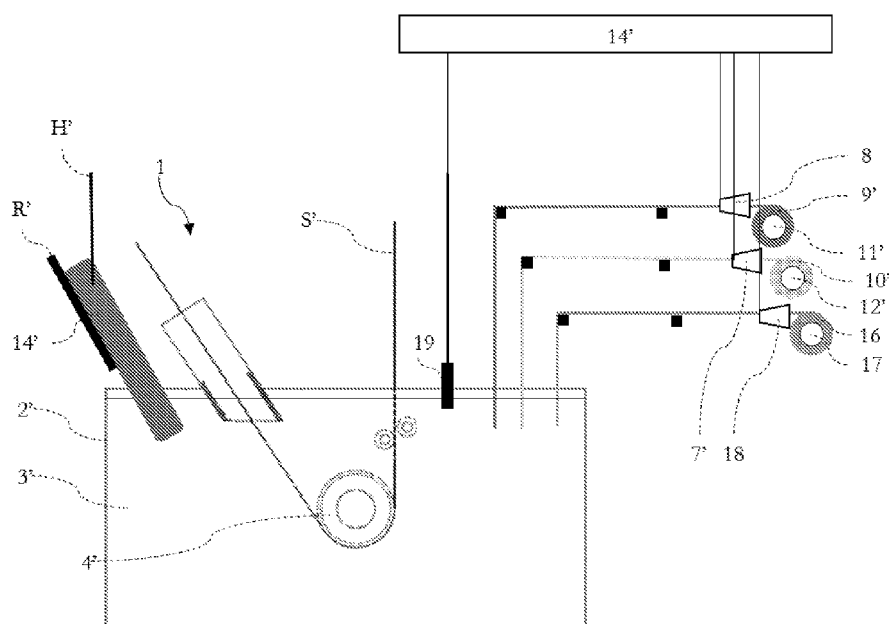


FIGURE 5

(57) Abstract: The present invention relates to a method and an equipment permitting to coat a substrate at a desired composition. It comprises a regulation system of the bath composition. It comprises means for inserting metallic wires or cored wires into the bath. Said metallic wires or cored wires can be composed of a single element or an alloy of several elements. The regulation system also comprises at least a mean measuring or estimating the bath composition.



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METAL WIRE INJECTION INTO A GALVANIZING BATH

The present invention relates to a method and an equipment permitting to coat a substrate with a coating at a desired composition.

In order to coat a substrate, several techniques can be used such as vapour deposition, electroplating or hot-dip. For example, in the case of hot-dip, a steel strip is passed through a coating tank containing a coating bath. The molten metal adheres to the steel strip and coats it. Depending on the bath composition and the strip nature, an intermetallic layer is formed between the coating and the strip. This intermetallic layer and the desired coating have different compositions. Consequently, the formation of this layer engenders a variation in the bath composition. Moreover, other parameters also affect the stability of the bath composition such as the oxidation at the bath surface and the formation of intermetallic compounds in the bath.

Patent EP 2 129 810 discloses a method to keep the initial proportion constant during the deposition by composition adjustment means of the metallic bath comprising means for supplying the evaporation means with molten metal alloy of controlled composition. In this patent, a composition variation is engendered during the coating due to the different vapor pressure of the components, i.e.: a Mg increase. In order to counter this drawback, liquid metal is brought to the crucible to continuously renew the tank.

However, by using the above method and its equipment, the bath composition of the examples is limited to only two elements because for each desired coating, the corresponding bath composition must be established in function of the different vapour pressures. Consequently, the process is not flexible due to the complexity of finding the right bath composition depending on the vapour pressures and the desired coating. Moreover, taking into account the area coated by the process and the need to do a vacuum, the coating speed of the whole process is limited.

Consequently, there is a need to find a way to easily and continuously coat a substrate with a predetermined alloy comprising at least three elements. Moreover, the process productivity should also be increased.

The purpose of this invention is to provide a solution solving the aforementioned problems.

This object is achieved by providing a method according to claim 1. The method can also comprise any characteristics of claims 2 to 8. This object is also achieved by providing an apparatus according to claims 9 to 11.

Other characteristics and advantages of the invention will become apparent from the following detailed description of the invention.

To illustrate the invention, various embodiments and trials of non-limiting examples will be described, particularly with reference to the following figure:

Figure 1 is a schematic view of an embodiment of a coating installation.

Figure 2 is a schematic cross-section view of a substrate, a coating layer and an intermetallic layer.

Figure 3 is a schematic view of an embodiment of a coating installation comprising an ingot being fed.

Figure 4 is a schematic view of an embodiment of a coating installation comprising a mean controlling the wire addition.

Figure 5 is a schematic view of a second embodiment of a coating installation.

The invention relates to a method for continuously coating a moving substrate S wherein a coating is continuously deposited on said substrate, by means of

- a coating installation 1 comprising a coating tank 2,
 - a molten metal alloy bath 3 inside said coating tank 2 and
 - means for conveying 4 said substrate through said tank 2,
 - said molten metal alloy bath having an initial predetermined composition comprising from 51% to 99% by weight of a first metal and from 1% to 49% by weight of cumulated amounts of at least a second and third metal,
 - the first, second and third metals being different from each other,
- comprising the steps of:

- feeding an ingot composed of at least 50.1% of said first metal
- repeatedly estimating or modelling the bath composition or and
- add a defined quantity, of at least said first, second and/or third metals, by means of wire injection into said molten metal alloy bath 3 permitting to keep each metal proportion at more or less 10% of its initial predetermined proportion in the course of coating.

As illustrated in Figure 1, the coating installation 1 comprises a coating tank 2, means for passing 4 a substrate S through said molten metal alloy bath 3. The means for conveying 4 a

substrate are generally a roll immersed in the molten metal alloy bath and means for conveying the substrate in and out of the bath (not represented). The substrate S is commonly a band or a strip or a wire.

The initial predetermined proportion of each metal is kept at more or less 10% of its initial predetermined proportion. It means that for example, if the initial predetermined proportion of a first metal is of 70.0%, its proportion can vary from 63.0% to 77.0% during the course of the coating and that if the predetermined proportion of a second metal is of 20.0%, its proportion can vary from 18% to 22% during the course of the coating.

Consequently, this invention easily and continuously coats a substrate with a predetermined alloy comprising at least three elements, increases the flexibility of the process and the process productivity compared to the state of the art.

As already explained, when the strip S passes through the molten metal alloy bath 3, the latter adheres to the strip and forms a desired coating having the same composition as the molten metal alloy bath. However, as illustrated in Figure 2, a monophasic or multiphasic intermetallic coating 5, having a different composition than the desired coating, can be formed between those two layers (the strip S and the desired coating 6). At least one of the element present in the molten metal alloy bath 3 has a higher concentration in the intermetallic layer 5 than in the molten metal alloy bath 3, such at least one element is considered as an overconsumed element. Even in this case, when at least an intermetallic layer is formed, the coating is considered as being deposited on said substrate. That is why, the intermetallic layer and the desired coating will be referred as the coating in the rest of the patent. In the course of the strip coating, this intermetallic layer 5 formation leads to a change in the composition of the molten metal alloy bath 3 because of their different composition. Moreover, other processes and/or phenomenon such as the oxidation at the metal molten alloy surface and the formation of intermetallic compounds in the bath also have an impact on the bath composition.

Therefore, means permitting to add a defined quantity of the said at least said first, second and/or third metals into said molten metal alloy bath 3 are used to compensate the composition change of the molten metal alloy bath happening in the course of the strip coating. So, the components proportion delivered by the means permitting to add a defined quantity of the said at least said first, second and/or third metals is different than the molten metal alloy bath

composition, e.g.: the overconsumed components proportion is higher in the delivered components than in the molten metal alloy bath.

The required quantity of wires to be added can be estimated or modelled using several parameters such as:

- the strip speed and dimensions,
- the intermetallic and coating thickness,
- the composition difference between the intermetallic, the coating and the bath,
- the melting rate and composition of potential ingots present in the tank 2,
- the process conditions,
- the formation rate and composition of intermetallic compound in the bath,
- the oxidation rate and reaction at the surface of the molten metal alloy bath.

The defined quantity of at least said first, second and/or third metals added into the molten metal alloy bath can be defined using the estimation of the bath composition and/or the model of the bath composition. Those quantities are defined such that each metal proportion is kept at more or less 10 % of its initial predetermined proportion in the course of coating. The term “defined” can be understood as “controlled”. Consequently, added quantities of first, second and/or third metals are controlled and defined.

As illustrated in Figure 1, said means permitting to add (7, 8) a defined quantity of said at least said first, second and/or third metals into said molten metal alloy bath 3 can be wire injectors. Each of them is pulling a metallic wire (9, 10) towards the molten metal alloy bath 3 and thus adding a desired quantity of said metallic wires into the molten metal alloy bath 3. The additions realised by the previously mentioned means must be precise enough to enable a constant maintenance of the bath composition and/or reach the desired bath composition at all time. The means permitting to add a defined quantity of said metal wires can be controlled manually or automatically.

Said metal wires are preferably wound or coiled around support means (11, 12) such as a spool or a reel or a bobbin. Said support means can be positioned above the tank but are preferably aside because the replacement of the wire coil is thus eased and safer. It is safer and eased because the replacement is not done above the molten metal alloy bath 3. Said metallic wires (9, 10) can be composed of a single element and/or an alloy of several metallic elements depending on the aimed bath composition. Said metallic wires can also be cored wires made of at least two different metals and/or alloys. The melting point of the wires is preferably below the molten metal

alloy bath temperature. Apparently, such a melting point allows a better melting of said wires compared to wires having a melting point above the molten metal alloy bath temperature.

The repeated bath composition measurements can be done by analysing frequent punctual bath samples and/or by an on-line continuous measurement device such as a Laser-Induced Breakdown spectroscope.

The right amount of the said at least said first, second and/or third added metals is introduced into the molten metal alloy bath based on a predictive model and/or the repeated bath composition measurements

Even more preferably, said ingot 13 has a composition close to the predetermined composition of the molten metal alloy bath, less than 5 wt% difference for each element compared to the initial predetermined composition of the molten metal alloy bath. Such an ingot permits to lower the wire consumption of the said at least said first, second and/or third added metals. In case the added metals are wires, it also eases the wire management because a smaller quantity is used and thus the replacement of the wires is less frequent. Preferably, as illustrated in Figure 3, the ingot is fed on a side of the tank 2, between the substrate and a tank wall. At least a part of the ingot is immersed into the molten metal alloy bath 3. Preferably the ingot lies on a support R, which can be a ramp, and is hold by a holding mean H, which can be a hook, said holding mean can be moved to immerse more or less the ingot.

Preferably, as illustrated in Figure 4, said coating installation comprises a management system 14

- controlling said means permitting to add a defined quantity (7, 8) of the said at least said first, second and/or third metals and
- having access to the repeated molten metal alloy bath composition measurements and/or composition evolution prediction models of said molten metal alloy bath and
- said means permitting to add a defined quantity of said metal wires are controlled automatically.

Such a management system 14 eases the regulation of the molten metal alloy bath 3 composition and should lower the risk of error during the wire addition compared to manually controlled wire addition.

Advantageously, said first metal is aluminium or zinc. Apparently, an aluminium based coating enhances the corrosion resistance because it acts as a barrier against the substrate corrosion while a zinc based coating wards off the oxidation.

Preferably, said molten metal alloy bath has an initial predetermined proportion from 70% to 95% by weight of said first metal. It permits to continuously coat on said substrate a layer of metal alloy based on a first metal and comprising a predetermined proportion of said first metal of from 70 to 95% by weight.

Advantageously, additional metals are zinc and/or silicon and/or magnesium and/or aluminium. Apparently, such additional metals when added in a certain range can enable the presence of sacrificial cathodic protection on the coated substrate as well as a better LME resistance as it can be seen in WO 2017/017521, WO 2017/017514 and WO 2017/017513.

Preferably, said substrate is a metallic strip. More preferably, said substrate is a steel strip.

Preferably, said metal wires are made of at least one of the following elements: aluminium and/or zinc and/or silicon and/or magnesium. More preferably, metal wire containing aluminium also contains zinc and/or silicon and/or magnesium to lower the fusion point in order to facilitate its melting and diffusion into the coating tank.

Preferably, said initial predetermined proportion of each metal is kept at more or less 1% of its initial predetermined proportion. Apparently, such a range increases the coating quality because the coating composition is more homogeneous

Optionally, the molten metal alloy bath comprises additional elements chosen from Sr, Sb, Pb, Ti, Ca, Mn, Sn, La, Ce, Cr, Zr or Bi, the content by weight of each additional element being inferior to 0.3% by weight and optionally residuals elements from feeding ingots or from a passage of a steel substrate in the molten bath including iron.

The invention also relates to an equipment 1 for continuously coating a substrate S according to the method of claim 1 comprising a coating tank 2 able to contain a molten metallic alloy bath 3 inside said coating tank 2, means for conveying 4 said substrate S through said molten metallic alloy bath 3, two metallic wires (9, 10) of different controlled composition and means

permitting to add a defined quantity (7, 8) of said metallic wires into said molten metal alloy bath 3 and measurement means of the molten metal alloy bath composition.

Preferably, as illustrated in Figure 4, said coating installation comprises a management system

- controlling 14 said means permitting to add (7, 8) a defined quantity of metallic wires into said molten metal alloy bath 3 and

- having access to the repeated molten metal alloy bath composition measurements and/or composition evolution prediction models of said molten metal alloy bath.

Preferably, said equipment comprises three metallic wires of different controlled composition and means permitting to add a defined quantity of said metallic wires into said molten metal alloy bath.

Preferably, said equipment comprises four metallic wires of different controlled composition and means permitting to add a defined quantity of said metallic wires into said molten metal alloy bath.

Preferably, as illustrated in Figure 5, using the teaching of the present invention, a tank 2' is filled with a molten metal alloy 3' and comprises an ingot being fed 13' into said molten metal alloy. It is desired to produce a coating on the substrate, a steel strip S', with the same composition as the one of the molten metal alloy.

Preferably the ingot lies on a ramp R' and is held by a hook H', said hook can be moved to immerse more or less the ingot.

Moreover, three metallic wires of different controlled composition (9', 10' and 16) are injected. Each wire is wound onto a bobbin (11', 12' and 17) and only one end of the wire is not wound but goes from the bobbin to the molten metal alloy bath 3'. Said bobbins are not placed directly above the bath but are spaced from it. Apparently, such a layout allows the workers to safely walk around the tank and not trip on the wire. Each metallic wire (6', 7' and 16) passes by a means permitting to add (8', 9', 18) a defined quantity of metallic wires, a wire injector. Each wire injector is connected to the management system 14' and can be controlled by the management system 14'. The means measuring repeatedly the bath composition is a Laser-Induced Breakdown spectroscope 19 connected to the management system 14'. Said management system controls, in function of the bath composition measurement and the prediction model of the bath composition,

the quantity of said metallic wires to inject into the bath in order to keep the bath proportion at more or less 0.5 wt% of its initial predetermined proportion in the course of coating

The invention has been described above as to the embodiment which is supposed to be practical as well as preferable at present. However, it should be understood that the invention is not limited to the embodiment disclosed in the specification and can be appropriately modified within the range that does not depart from the gist or spirit of the invention, which can be read from the appended claims and the overall specification, and a manufacturing method of a hot-rolled steel sheet and a manufacturing apparatus of a hot-rolled steel sheet with such modifications are also encompassed within the technical range of the invention.

CLAIMS

1. Method for continuously coating a moving substrate S wherein a coating is continuously deposited on said substrate, by means of a coating installation (1) comprising a coating tank (2), a molten metal alloy bath (3) inside said coating tank (2) and means for conveying (4) said substrate through said tank (2), said molten metal alloy bath having an initial predetermined composition comprising from 51% to 99% by weight of a first metal and from 1% to 49% by weight of cumulated amounts of at least a second and third metal, the first, second and third metals being different from each other, comprising the steps of:
 - feeding an ingot composed of at least 50.1% of said first metal
 - repeatedly estimating or modelling the bath composition or and
 - add a defined quantity, of at least said first, second and/or third metals, by means of wire injection into said molten metal alloy bath (3) permitting to keep each metal proportion at more or less 10% of its initial predetermined proportion in the course of coating.
2. Method according to claim 1, wherein said coating installation comprises a management system 14 controlling said means permitting to add a defined quantity (7, 8) of the said at least said first, second and/or third metals and having access to the repeated molten metal alloy bath composition measurements and/or composition evolution prediction models of said molten metal alloy bath and said means permitting to add a defined quantity of said metal wires are controlled automatically.
3. Method according to claim 1 or 2, wherein said initial predetermined proportion of each metal is kept at more or less 1% of its initial predetermined proportion
4. Method according to anyone of claim 1 to 3, wherein said first metal is aluminium or zinc.
5. Method according to anyone of claim 1 to 4, wherein said molten metal alloy bath has an initial predetermined proportion of from 70% to 95% by weight of said first metal.
6. Method according to anyone of claim 1 to 5, wherein said at least two additional metals are zinc and/or silicon and/or magnesium and/or aluminium.

7. Method according to anyone of claim 1 to 6, wherein said substrate is a steel strip.
8. Method according to anyone of claim 1 to 7, wherein said at least two metal wires are made of at least one of the following elements: aluminium, zinc, silicon and magnesium.
9. An equipment (1) for continuously coating a substrate (S) according to the method of claim 1 comprising a coating tank (2) able to contain a molten metallic alloy bath (3) inside said coating tank (2), means for conveying (4) said substrate (S) through said molten metallic alloy bath (3), two metallic wires (9, 10) of different controlled composition and means permitting to add a defined quantity (7, 8) of said metallic wires into said molten metal alloy bath (3) and measurement means of the molten metal alloy bath composition.
10. An equipment according to claim 9, wherein said coating installation comprises a management system controlling (14) said means permitting to add (7, 8) a defined quantity of metallic wires into said molten metal alloy bath (3) and having access to the repeated molten metal alloy bath composition measurements and/or composition evolution prediction models of said molten metal alloy bath.
11. An equipment according to claim 9 or 10, wherein said equipment comprises three metallic wires of different controlled composition and means permitting to add a defined quantity of said metallic wires into said molten metal alloy bath.

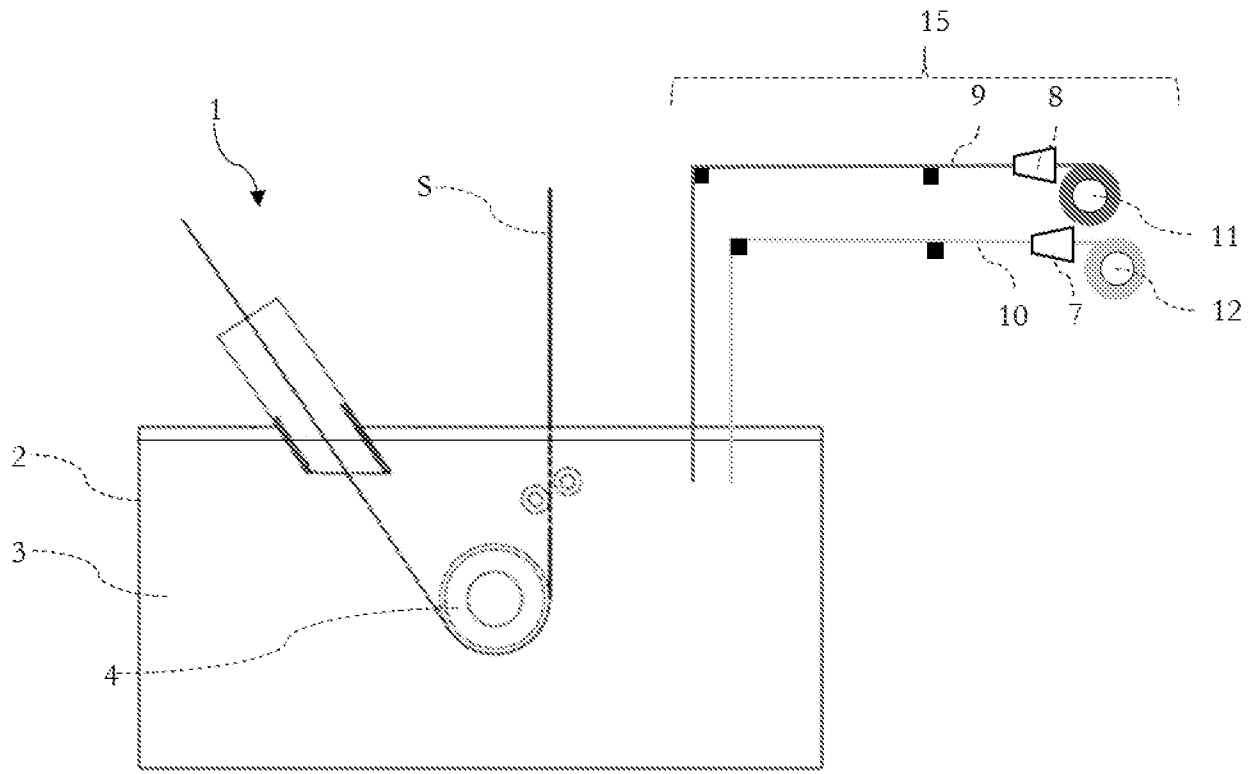


FIGURE 1

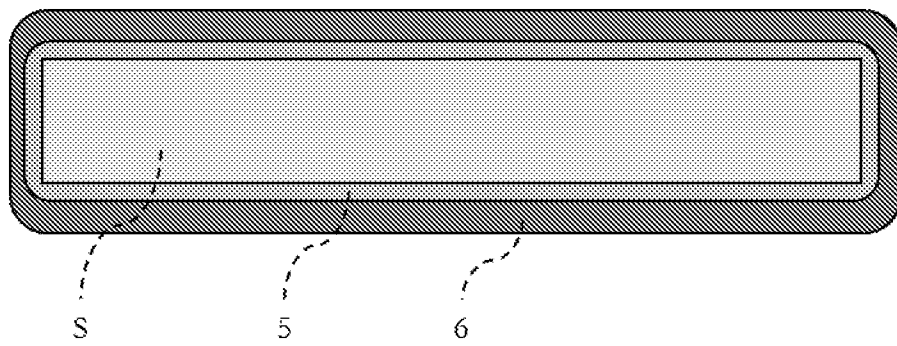


FIGURE 2

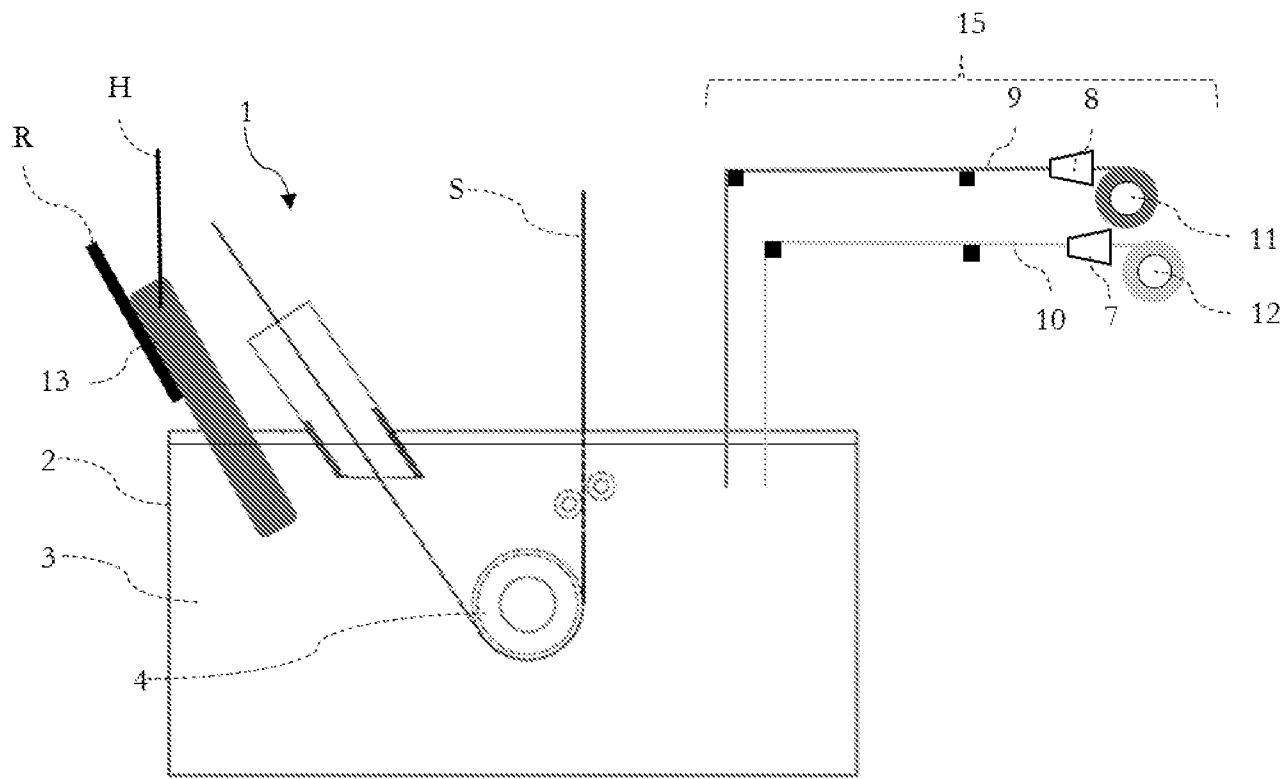


FIGURE 3

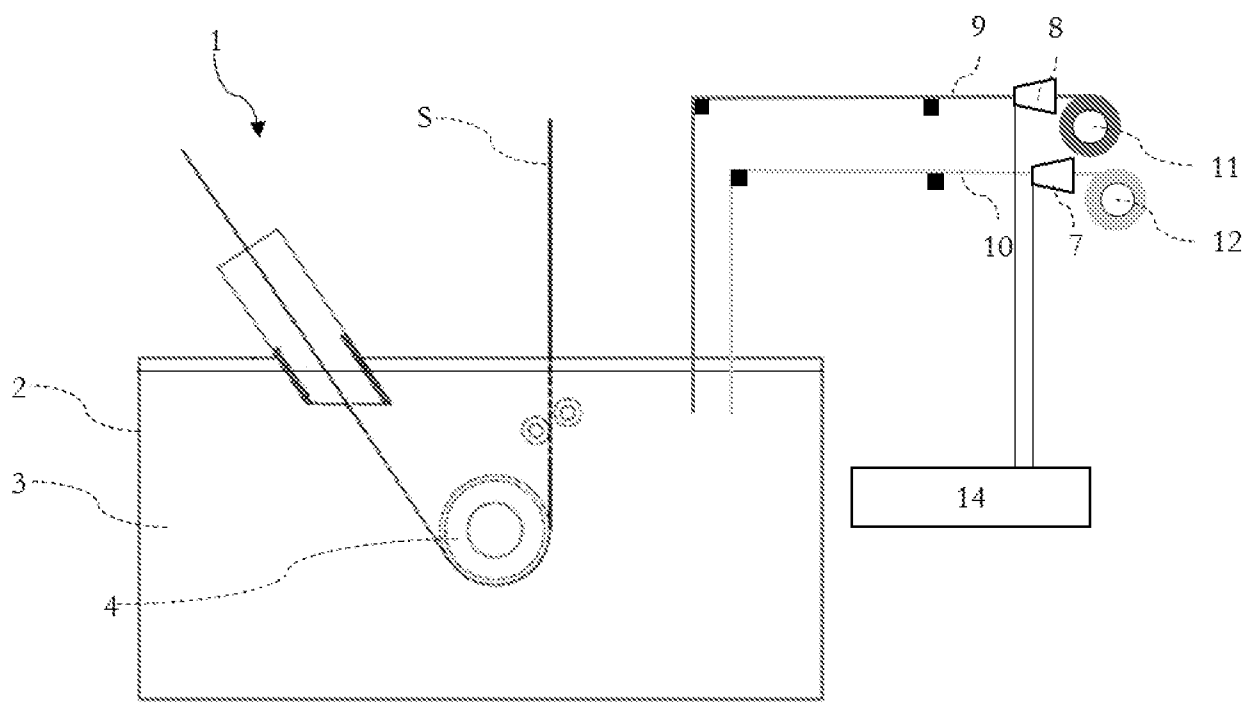


FIGURE 4

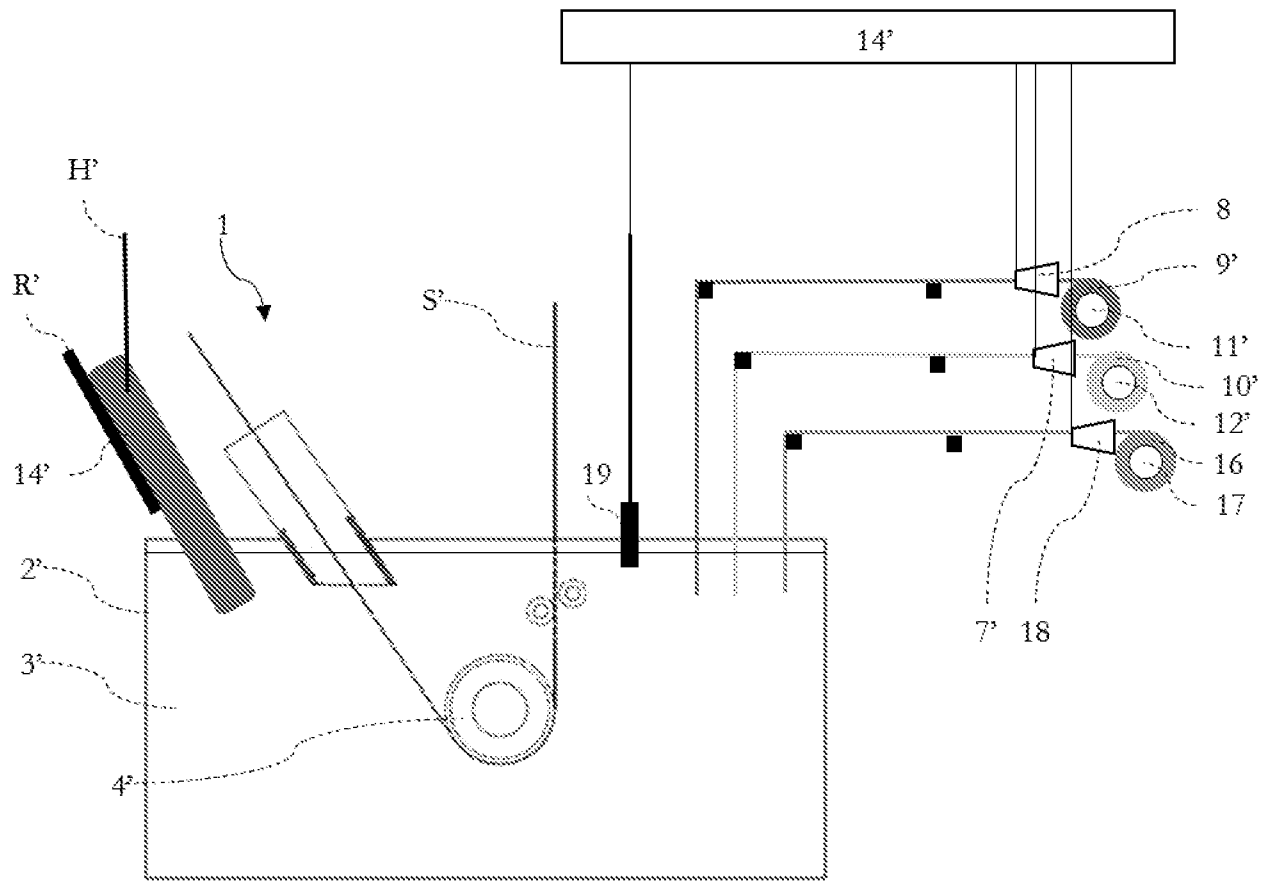


FIGURE 5

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2019/059977

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C2/00 C23C2/06 C23C2/12 C23C2/40
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/053184 A2 (SPECIALTY MINERALS MICHIGAN [US]; KELLY PAUL ALLAN [US]) 24 June 2004 (2004-06-24) page 1, lines 1 - 19; claims 1-15 page 7, lines 10 - 12 page 7, line 21 - page 8, line 4 page 10, lines 11 - 13; table 1 -----	1-11
A	KR 2004 0057746 A (POSCO) 2 July 2004 (2004-07-02) page 3. 4; figure 3 -----	1-11
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A	US 5 827 576 A (CARTER WILLIAM A [US] ET AL) 27 October 1998 (1998-10-27) abstract; figure 1 -----	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

17 January 2020

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29/01/2020

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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