## (11) EP 3 835 460 A1

(12)

# EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication: 16.06.2021 Bulletin 2021/24

(21) Application number: 19846998.3

(22) Date of filing: 24.05.2019

(51) Int CI.: C25D 7/00 (2006.01) E03C 1/042 (2006.01)

C25D 3/12 (2006.01)

(86) International application number: **PCT/JP2019/020627** 

(87) International publication number: WO 2020/031462 (13.02.2020 Gazette 2020/07)

(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

KH MA MD TN

(30) Priority: 10.08.2018 JP 2018152107

(71) Applicant: LIXIL Corporation

Koto-ku

Tokyo 136-8535 (JP)

(72) Inventors:

 ITO Keiji Tokyo 136-8535 (JP)

 NISHIKAWA Takeshi Tokyo 136-8535 (JP)

(74) Representative: Grünecker Patent- und

Rechtsanwälte PartG mbB Leopoldstraße 4

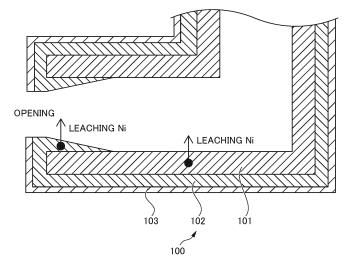
80802 München (DE)

#### (54) TOOL FOR WATER SUPPLY SERVICE

(57) The purpose of the present invention is to provide a tool for water supply, which has luster and rarely undergoes the leaching out of nickel. A tool for water supply 100 which is provided with a nickel-plated layer 102 formed on a base material 101, wherein the nickel-plated layer 102 contains no sulfur component, the

corrosion potential of the nickel-plated layer 102 in a leaching solution as measured against a saturated calomel electrode is -0.01 or more (preferably +0.04 V or more), and the Wa value of the nickel-plated layer 102 as measured using a WaveScan device manufactured by BYK is 5.1 or less.

FIG.3



EP 3 835 460 A1

#### Description

30

40

45

55

#### **TECHNICAL FIELD**

[0001] The present invention relates to a technique to reduce leaching of nickel from a device for water supply including a nickel plating layer formed on a base material.

#### **BACKGROUND ART**

- 10 [0002] Conventionally, devices for water supply that are used as a kitchen faucet, a laboratory faucet, a bath faucet, and other similar devices are made of, for example, a copper alloy from the viewpoints of corrosion resistance, processability, machinability, etc. This type of device for water supply is produced through a process in which a rough-formed copper alloy piece is cut and ground to be formed into a base material, and nickel plating is provided on the outer peripheral surface of the base material. In some cases, chrome plating is also provided on the nickel plating.
- 15 [0003] As shown in FIG. 3, in the vicinity of an opening of such a device for water supply provided with nickel plating, the nickel plating layer may also be deposited on the inner surface of the device for water supply so as to have an overlay portion due to throwing power. Even if chrome plating is provided on the device for water supply, the chrome plating is unlikely to be deposited on the inner surface. Referring to the device 100 for water supply shown in FIG. 3, when the base material 101 comes into contact with water, nickel not only leaches from the base material 101 (which often contains 20 nickel intentionally added for the purpose of increasing corrosion resistance or nickel as an unintentional impurity), but also from the overlay portion of the nickel plating layer 102.
  - [0004] Specifically, as shown in FIG. 4, an analysis of components of a cross section of an opening of a known device for water supply provided with nickel plating has demonstrated the following. In a region inwardly distant by more than 15 mm from the end face of the opening (inner region of the device for water supply), the principal component (copper) of the base material 101 is detected at a high ratio, whereas negligible nickel is detected. On the other hand, in a region inwardly extending over a distance of less than 15 mm from the end face of the opening (region close to the opening of the device for water supply), nickel leaching from the overlay portion is detected at a high ratio.
  - [0005] In view of this, a technique is proposed to reduce an amount of nickel leaching from nickel plating provided on a device for water supply (in particular, the overlay portion) (see, for example, Patent Document 1). According to the technique disclosed in Patent Document 1, a sulfur component-containing organic additive is added to the nickel plating to impart gloss to the device for water supply, while chloral hydrate is added to reduce an amount of nickel leaching into tap water. According to this technique, chloral hydrate is added to a nickel plating processing solution to which the sulfur component-containing organic additive has been added, so that the nickel plating has a noble potential and the amount of nickel leaching from the nickel plating is reduced.
- 35 [0006] Meanwhile, water quality that tap water needs to maintain is determined by an Ordinance of the Ministry of Health, Labour, and Welfare, pursuant to the Water Supply Law. "Ministerial Ordinance on Water Quality Standards" enforced on April 1, 2015 provides items of water quality standards and standard values (51 items). The Ministerial Ordinance also provides target-setting items for water quality management and target values (26 items), as a target of water quality that tap water should maintain. Nickel constitutes one item of the target-setting items for water quality management, and its target value is set to 0.02 mg/L.
  - [0007] The target values for water quality management provided in the Ministerial Ordinance are predicted to be regarded as water quality standards required for potable water. In this case, it will be required that an amount of nickel (a leaching value of nickel) contained in potable water discharged from a device for water supply be not more than onetenth of the value defined in the target-setting item for water quality management. The same or similar measures will be needed for tap water other than potable water.
  - [0008] Patent Document 1: Japanese Unexamined Patent Application, Publication No. 2015-212417

#### DISCLOSURE OF THE INVENTION

50 Problems to be Solved by the Invention

> [0009] However, the nickel plating (hereinafter also referred to as "gloss nickel plating") disclosed in Patent Document 1, to which the sulfur component-containing organic additive is added, can reduce an amount of leaching nickel to a limited extent. On the other hand, use of nickel plating to which no sulfur component-containing organic additive is added (hereinafter also referred to as "semigloss nickel plating") can reduce an amount of leaching nickel, while making it difficult to attain sufficient gloss.

> [0010] It is an object of the present invention to provide a device for water supply which is glossy and from which a small amount of nickel leaches.

#### Means for Solving the Problems

**[0011]** The present invention related to a device for water supply including a nickel plating layer formed on a base material. The nickel plating layer contains no sulfur component. A corrosion potential of the nickel plating layer in a leach test liquid is -0.01 V or greater with respect to a saturated calomel electrode as a reference. A surface of the nickel plating layer has a Wa value of 5.1 or less.

**[0012]** The corrosion potential of the nickel plating layer in the leach test liquid is preferably +0.04 V or greater with respect to the saturated calomel electrode as the reference.

#### 10 Effects of the Invention

[0013] The present invention provides a device for water supply which is glossy and from which a small amount of nickel leaches.

#### 15 BRIEF DESCRIPTION OF THE DRAWINGS

#### [0014]

20

30

50

- FIG. 1 is a schematic view showing a device for water supply according to the present embodiment;
- FIG. 2 is an exploded view of the device for water supply according to the present embodiment;
- FIG. 3 is a schematic cross-sectional view illustrating a structure of the vicinity of an opening of the device for water supply according to the present embodiment;
- FIG. 4 is a graph showing detection ratios of metals at an inner surface of an opening of a known device for water supply;
- FIGS. 5A and 5B show representative results of analyses of Examples and Comparative Examples using an EPMA; FIGS. 6A and 6B shows, on an enlarged scale, sulfur peaks in FIGS. 5A and 5B;
  - FIG. 7 shows a relationship between an appearance of a nickel plating layer and a Wa value (measured with WaveScan of BYK) of a surface of the nickel plating layers of Examples and Comparative Examples;
  - FIG. 8 shows potential-current curves and Ni leaching values of representative plating layers in a leach test liquid; and FIG. 9 shows a relationship between a corrosion potential and a nickel leaching value of representative nickel plating layers in a leach test liquid.

#### PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0015] A preferred embodiment of the present invention will be described with reference to the drawings. Note that the present invention is not limited to the following embodiment.

[0016] First, a faucet produced by combining devices for water supply according to the present embodiment will be described as an example. FIG. 1 is a schematic view showing the faucet according to the present embodiment. FIG. 2 is an exploded view of the faucet according to the present embodiment. As shown in FIGS. 1 and 2, the faucet 1 according to the present embodiment is a common faucet (e.g., a kitchen faucet, a lavatory faucet, or a bath faucet) and configured to discharge tap water from a spout 30. The faucet 1 includes a body 10, legs 20, and handles 50. In the present specification, the term "device for water supply" has a meaning encompassing not only faucet parts such as a tap and a valve for supplying potable water, but also a joint and a water supply pipe. The "devices for water supply" are classified into "end-use water supply devices", "water supply pipes", "water supply devices disposed at middle positions of piping", etc. The term "device for water supply" as used herein encompasses all of these devices and pipes. Structurally speaking, the "device for water supply" has an internal channel through which water passes and an exterior surface which does not contact with water. The present invention can be favorably provided as a faucet part.

**[0017]** The body 10 is an example of the devices for water supply connectable to various devices for water supply. The body 10 includes a threaded portion 12 connectable to the leg 20, a threaded portion 13 connectable to the spout 30, and a threaded portion 14 connectable to the handle 50 via a spindle 40.

[0018] The leg 20 is an example of the devices for water supply connectable to the body 10. The leg 20 has one end connected to a tap water supply source (not shown). The other end of the lag 20 has a nut 21 attached thereto. The nut 21 of the leg 20 is screwed onto the threaded portion 12 of the body 10, so that the leg 20 is connected to the body 10. [0019] The spout 30 is an example of the devices for water supply connectable to the body 10. One end of the spout 30 has a nut 31 attached thereto, and the other end has an end sleeve 32 attached thereto. The nut 31 of the spout 30 is screwed onto the threaded portion 13 of the body 10, so that the spout 30 is connected to the body 10.

**[0020]** The handle 50 is a part for adjusting a flow rate of water to be discharged. One end of the spindle 40 is attached to the handle 50. The other end of the spindle 40 is screwed onto the threaded portion 14 of the body 10, so that the

handle 50 is connected to the body 10 via the spindle 40.

30

35

50

**[0021]** The body 10, the leg 20, the nut 21, the spout 30, the nut 31, the end sleeve 32, and the spindle 40 include a base material 101 and a nickel plating layer 102 formed on an outer peripheral surface of the base material 101. In the present embodiment, the body 10, the leg 20, the nut 21, the spout 30, the nut 31, and the end sleeve 32 include a chrome plating layer 103 formed on the nickel plating layer 102. The body 10, the leg 20, the spout 30, and other components have undergone lead removal treatment as necessary.

**[0022]** Next, the device for water supply according to the present embodiment will be described. FIG. 3 is a schematic view illustrating a structure of the device for water supply according to the present embodiment, specifically, a cross-sectional structure of an opening of the body 10 as the device for water supply. FIG. 4 is a graph showing detection ratios of metals at an inner surface of an opening of a known device for water supply.

**[0023]** As shown in FIG. 3, the device 100 for water supply according to the present embodiment includes the nickel plating layer 102 formed on the base material 101. In the opening of the device 100 for water supply, the nickel plating spreads to reach the water channel so as to have an overlay portion due to throwing power. In the device 100 for water supply having this configuration, when water flows in an F1 direction, nickel leaches not only from the base material 101, but also from the overlay portion of the nickel plating layer 102.

**[0024]** As shown in FIG. 4, conventionally, the amount of nickel leaching from the base material 101 is less than the amount of nickel leaching from the overlay portion of the nickel plating layer 102. Therefore, a reduction in the leaching of nickel from the device 100 for water supply requires a reduction in the leaching of nickel from the overlay portion of the nickel plating layer 102. It would be conceivable to provide the chrome plating layer 103 on the nickel plating layer 102. However, since the chrome plating layer 103 is unlikely to spread inward and does not contain nickel, the presence or absence of the chrome plating layer 103 has a small effect on the leaching of nickel.

**[0025]** In the present embodiment, the base material 101 is made of, for example, a copper alloy. The nickel plating layer 102 is a layer formed on the base material 101. The nickel plating layer 102 is formed on the base material 101 by using, for example, a plating solution having the composition and condition described below. The chrome plating layer 103 may be provided on the nickel plating layer 102.

**[0026]** A basic composition of the nickel plating solution, which is the so-called Watts solution, includes nickel ions, chloride ions, sulfate ions, and boric acid. Specifically, the basic composition includes, for example, 50 g/L of NiCl<sub>2</sub>·6H<sub>2</sub>O, 290 g/L of NiSO<sub>4</sub>·6H<sub>2</sub>O, and 40 g/L of H<sub>3</sub>BO<sub>3</sub>. The plating is formed under the conditions of a pH of about 4.0 and a temperature of about  $55^{\circ}$ C. As organic additives, sulfur-free salicylic acid, hexynediol, butynediol, propargyl alcohol, chloral hydrate, etc. can be used.

**[0027]** The plating solution described above is free of sulfur-containing organic additives (e.g., saccharin). Consequently, the nickel plating layer 102 of the present embodiment contains no sulfur. This feature reduces leaching of nickel from the nickel plating layer 102. In the present specification, "a nickel plating layer contains no sulfur" refers to a case where sulfur is not detected in an elementary analysis using an EMPA (e.g., an analysis method to be described later) performed on the nickel plating layer.

**[0028]** Further, if the nickel plating layer that has been formed using the above-described plating solution has a corrosion potential of +0.04 V or greater with respect to a saturated calomel electrode (SCE) in a leach test liquid, the amount of nickel leaching into tap water from the device for water supply can be reduced to no more than one-tenth of the value defined in the target-setting item for water quality management.

**[0029]** Specifically, when 0.8 g/L or more (preferably 0.9 g/L or more) of chloral hydrate is added to the plating solution, the nickel plating layer 102 has a noble potential, and the leaching of nickel from the nickel plating layer 102 is further reduced. On the other hand, when the amount of chloral hydrate contained in the plating solution is less than 0.8 g/L, it is difficult to reduce the leaching of nickel by the chloral hydrate alone.

[0030] Further, use of the plating solution described above makes the nickel plating layer have a Wa value of 5.1 or less as measured with WaveScan manufactured by BYK. As a result, the surface of the device 100 for water supply (the surface of nickel plating layer 102) is provided with gloss. Specifically, addition of 0.8 g/L to 1.75 g/L of chloral hydrate to the plating solution makes the surface of the device 100 for water supply glossy. On the other hand, when the amount of chloral hydrate in the plating solution exceeds 1.75 g/L, the surface of the device 100 for water supply becomes tarnished. Note that in the present specification, the Wa value is measured with the WaveScan manufactured by BYK.

**[0031]** As can be seen, by a production method including forming plating on the base material 101 using a nickel plating processing solution that is free of sulfur-containing organic additives and contains chloral hydrate in an amount of 0.8 g/L to 1.75 g/L, the device 100 for water supply can be produced which is glossy and from which a small amount of nickel leaches.

[0032] The present embodiment exerts the following effects. The device for water supply according to the present embodiment is configured as the device 100 for water supply including the nickel plating layer 102 provided on the base material 101. The nickel plating layer 102 contains no sulfur. A corrosion potential of the nickel plating layer 102 in the leach test liquid is -0.01 V or greater with respect to a saturated calomel electrode as a reference. A surface of the nickel plating layer 102 has a Wa value (as measured with the WaveScan manufactured by BYK) of 5.1 or less. This feature

enables provision of the device 100 for water supply which is glossy and from which a small amount of nickel leaches. [0033] The corrosion potential of the nickel plating layer in the leach test liquid is preferably +0.04 V or greater with respect to the saturated calomel electrode as the reference. This feature makes it possible to reduce an amount of nickel leaching into tap water from the device for water supply to no more than one-tenth of the value defined in the targetsetting item for water quality management.

[0034] Note that the present invention is not limited to the embodiment described above, but encompasses modifications and improvements made within the range in which the object of the present invention can be achieved.

[0035] For example, equivalent effects are exerted by application of the present invention to a device for water supply including a nickel plating layer having no chrome plating layer formed thereon. The body of the device for water supply may be subjected to lead removal treatment as necessary.

#### **EXAMPLES**

5

10

15

20

25

30

35

40

45

50

55

<Examples 1 to 5 and Comparative Examples 1 to 10>

[0036] Bodies of devices for water supply of Examples and Comparative Examples were produced according to plating condition Nos. 1 to 15 shown in.

		[Table 1]		
Example/ Comparative Example	Condition	Amount of Added Saccharin (g/L)	Amount of Added Chloral Hydrate (g/L)	Base Plating Solution
Example1	Condition No. 1	-	0.9	Semigloss Ni Plating
Comparative Example1	Condition No. 2	5.0	1.0	Gloss Ni Plating
Example2	Condition No. 3	-	0.2	Semigloss Ni Plating
Example3	Condition No. 4	-	0.4	Semigloss Ni Plating
Example4	Condition No. 5	-	0.8	Semigloss Ni Plating
Example5	Condition No. 6	-	1.25	Semigloss Ni Plating
Comparative Example2	Condition No. 7	5.0	-	Ultra-Gloss Ni Plating
Comparative Example3	Condition No. 8	5.0	-	Gloss Ni Plating
Comparative Example4	Condition No. 9	-	1.8	Semigloss Ni Plating
Comparative Example5	Condition No. 10	-	1.9	Semigloss Ni Plating
Comparative Example6	Condition No. 11	-	2.0	Semigloss Ni Plating
Comparative Example7	Condition No. 12	-	-	Semigloss Ni Plating
Comparative Example8	Condition No. 13	5.0	3.0	Gloss Ni Plating
Comparative Example9	Condition No. 14	-	-	Semigloss Ni Plating

(continued)

Example/ Comparative Example	Condition	Amount of Added Saccharin (g/L)	Amount of Added Chloral Hydrate (g/L)	Base Plating Solution
Comparative Example10	Condition No. 15	5.0	5.0	Gloss Ni Plating

#### <EPMA Analysis>

5

10

15

20

25

30

35

40

45

50

55

**[0037]** The bodies of the devices for water supply of Examples and Comparative Examples were each subjected to an analysis using an EPMA. FIG. 5A shows a representative result of the analyses of the condition Nos. 2, 7, 8, 13, and 15 in which the plating solution contained saccharin. FIG. 5B shows a representative result of the analyses of the condition Nos. 1, 3 to 6, 9 to 12, and 14 in which the plating solution did not contain saccharin. FIG. 6A shows, on an enlarged scale, the peak of sulfur in FIG. 5B.

**[0038]** As shown in FIGS. 5 and 6, the condition Nos. 2, 7, 8, 13, and 15 correspond to the so-called gloss nickel plating containing a sulfur component added thereto. The condition Nos. 1, 3 to 6, 9 to 12, and 14 correspond to the so-called semigloss nickel plating containing no sulfur component. In comparison with the gloss nickel plating, the semigloss nickel plating, which contains no sulfur component, allows a smaller amount of nickel to leach.

#### <Appearance Observation>

[0039] Surfaces of the devices for water supply produced under condition Nos. 1 to 15 were visually observed. Among the devices for water supply, devices that were as glossy as or glossier than the device for water supply of the condition No. 8 (gloss nickel plating; Comparative Example 5) are marked with a circle ("o"). The devices for water supply of the condition Nos. 12 and 14 (semigloss nickel plating containing no chloral hydrate) were not glossy, and the devices for water supply of the condition Nos. 9 to 11 had a tarnished surface. These devices for water supply were marked with a cross (" $\times$ "). A triangle (" $\Delta$ ") denotes devices for water supply having an intermediate degree of gloss between those marked with the circle ("o") and those marked with the cross (" $\times$ "). Further, the surface of each device for water supply was measured with the WaveScan of BYK. A relationship between the appearance and the Wa value is shown in FIG. 7. [0040] As shown in FIG. 7, it has been confirmed that the gloss of the surface of the body 10 for water supply increases with a decrease in the Wa value of the surface of the device 100 for water supply. Specifically, it has been confirmed that when the Wa value is 5.1 or less, the gloss of the surface is high enough so that device for water supply has an appearance suitable as a product. Further, it has been confirmed that when the Wa value of the surface is 3.6 or less, the device for water supply has gloss comparable to that of the gloss nickel plating.

#### <Ni Leaching Value and Corrosion Potential>

**[0041]** The devices for water supply produced using the Ni plating of the condition Nos. 1, 2, 5 to 8, and 12 were each subjected to the following conditioning and leach test in conformity with the method described in JIS S 3200-7 "Equipment for water supply service - Test methods of effect to water quality".

- (1) The device for water supply was washed with tap water for 1 hour, and then, washed with water three times.
- (2) A leach test liquid at a temperature of about 23°C was prepared. The inside of the device for water supply was filled with the leach test liquid and hermitically sealed. After the device for water supply was left standing for 2 hours, the liquid was disposed of. This operation was repeated four times.
- (3) The device for water supply was filled with the leach test liquid and hermitically sealed. After the device for water supply was left standing for 16 hours, the liquid was disposed of.
- (4) The operations (2) and (3) were repeated three times.
- (5) After the operation (2) was performed, the device for water supply was left standing for 64 hours, and then, the liquid was disposed of.
- (6) The operations (2) to (5) were performed once more.
- (7) The operations (2) to (4) were repeated three times, and thereafter, the operation (2) was carried out.
- (8) The device for water supply was filled with the leach test liquid and hermitically sealed. The device for water supply was then left standing for 16 hours, and all of the liquid was collected as a sample liquid.
- (9) A Ni concentration in the sample liquid was determined using a common inductively-coupled plasma emission spectrophotometry.

- (10) A calculation was performed using the Ni concentration of the sample liquid and a capacity of the tested device for water supply, so that the Ni concentration was converted to a Ni concentration in 1 L of water and a leaching value was determined. Note that the leach test liquid used in the leach test was specially prepared according to JIS S 3200-7.
- By way of the operations described above, a nickel leaching value was determined for each of the nickel plating layers produced under the condition Nos. 1, 2, 5 to 8, and 12 (Example 1, Comparative Example 1, Examples 4 and 5, and Comparative Examples 2, 3, and 7). Note that since the different types of devices for water supply have different capacities, the leaching values were calculated according to a predetermined conversion formula. Subsequently, the following operations were carried out.
  - (11) A specimen was cut off from an inner portion of the body 10 of the device for water supply where the Ni plating was deposited. A copper-coated wire was bonded to the specimen, and then, the specimen was coated with an adhesive such that only the Ni plating was exposed, whereby specimen was formed into a sample electrode.
  - (12) The sample electrode, a platinum electrode (counter electrode), and a saturated calomel electrode as a reference electrode were placed in the leach test liquid. A potential-current curve of the sample electrode was determined using a potentiostat. Here, a potential at which a current of 0.001 mA was observed was defined as a corrosion potential.

**[0042]** By way of the above-described operations, a corrosion potential in the leach test liquid was determined for each of the plating layers of the condition Nos. 1, 2, 5 to 8, and 12 (Example 1, Comparative Example 1, Examples 4 and 5, and Comparative Examples 2, 3, and 7). FIG. 8 shows the potential-current curves and the Ni leaching values of the plating layers of Examples 1, 4, and 5, and Comparative Examples 1 to 3 and 7 measured in the leach test liquid. FIG. 9 shows a relationship between the corrosion potential and the nickel leaching value of the plating layers of Examples 1, 4, and 5, and Comparative Examples 1 to 3 and 7 measured in the leach test liquid.

[0043] As shown in FIG. 8, it has been confirmed that the nickel leaching value decreases with an increase in the corrosion potential of the nickel plating layer. Specifically, it has been confirmed that when the corrosion potential is -0.01 V (with respect to the SCE) or greater, and preferably +0.02 V (with respect to the SCE) or greater, the nickel leaching value is reduced to lower than that of semigloss nickel plating that contains no chloral hydrate. Further, it has been confirmed that when the corrosion potential is +0.04 V (with respect to the SCE) or greater, the amount of nickel leaching into tap water from the device for water supply can be reduced to no more than one-tenth of the value defined in the target-setting item for water quality management.

#### EXPLANATION OF REFERENCE NUMERALS

#### [0044]

35

40

5

10

15

20

25

30

100: Device for Water Supply

101: Base Material

102: Nickel Plating Layer

#### **Claims**

- 1. A device for water supply comprising a nickel plating layer formed on a base material, wherein the nickel plating layer contains no sulfur component,
- wherein a corrosion potential of the nickel plating layer in a leach test liquid is -0.01 V or greater with respect to a saturated calomel electrode as a reference, and wherein a surface of the nickel plating layer has a Wa value of 5.1 or less.
  - wherein a surface of the flicker plating layer has a wa value of 5.1 of less
- 2. The device for water supply according to claim 1, wherein the corrosion potential of the nickel plating layer in the leach test liquid is +0.04 V or greater with respect to the saturated calomel electrode as the reference.

55

# FIG .1

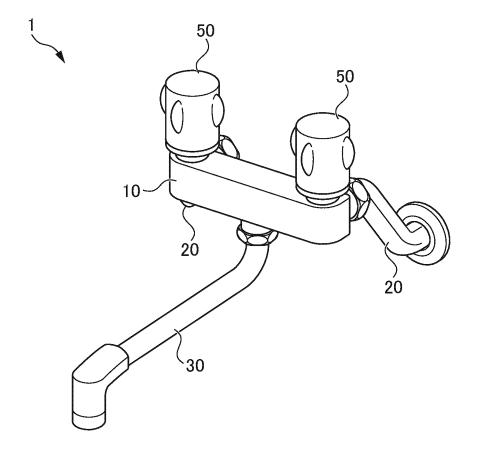


FIG .2

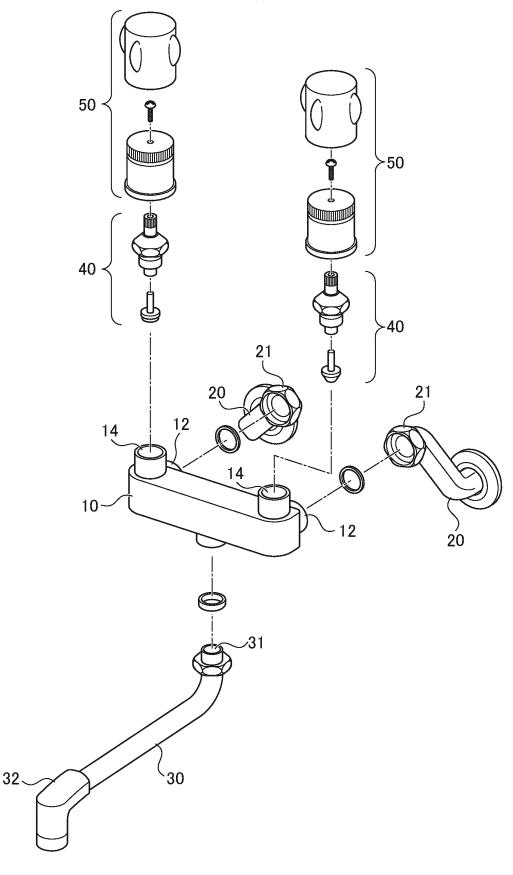


FIG .3

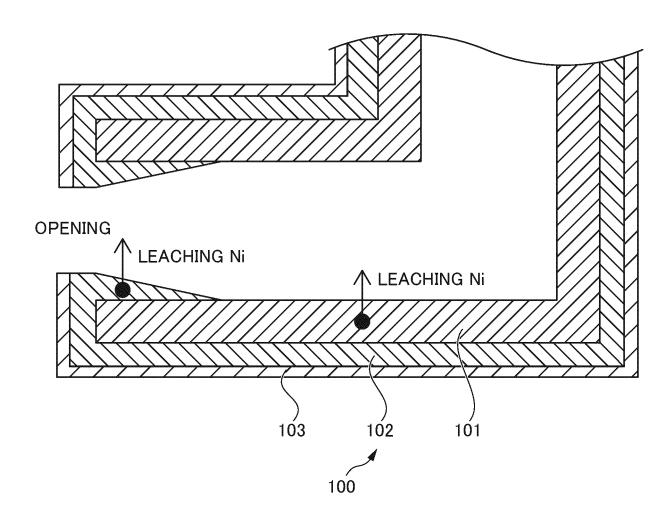


FIG .4

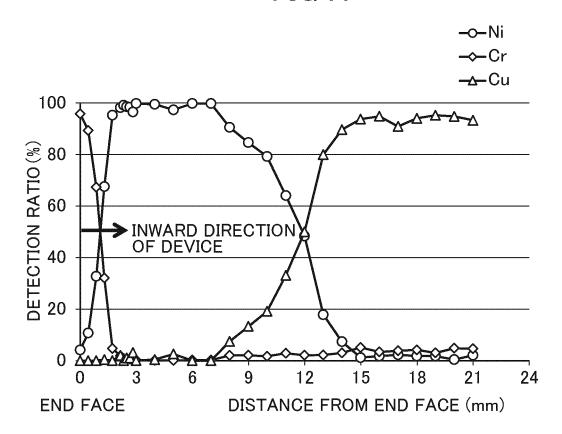
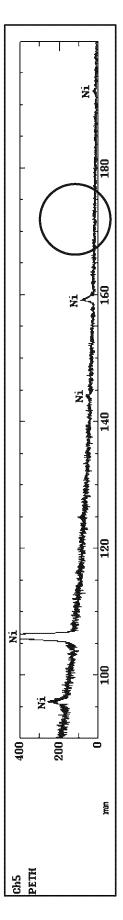
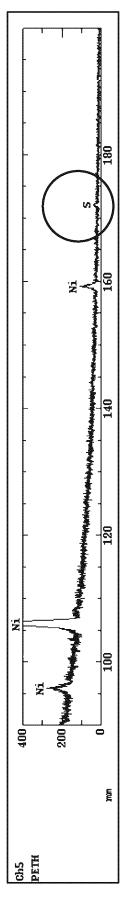


FIG .5A



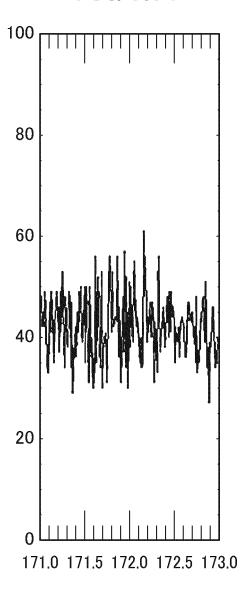
SULFUR IS NOT DETECTED

FIG. 5B

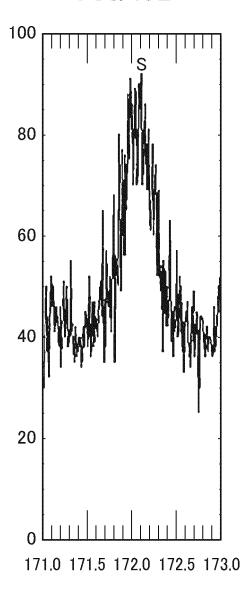


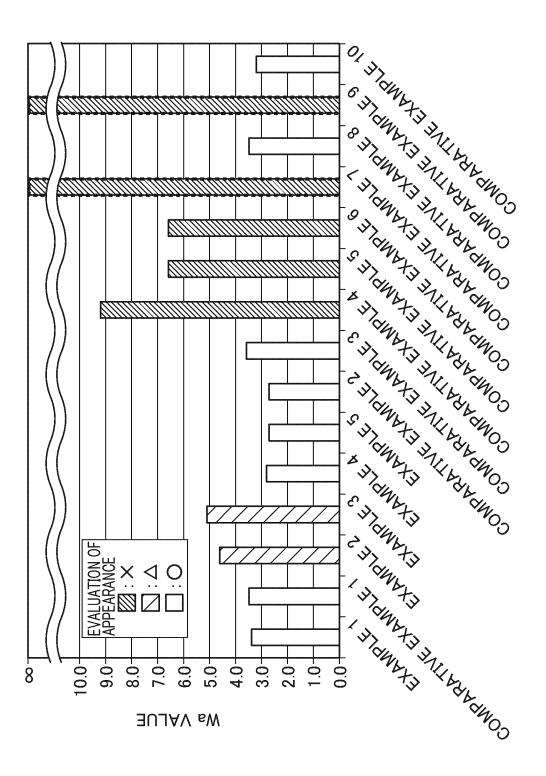
SULFUR IS DETECTED



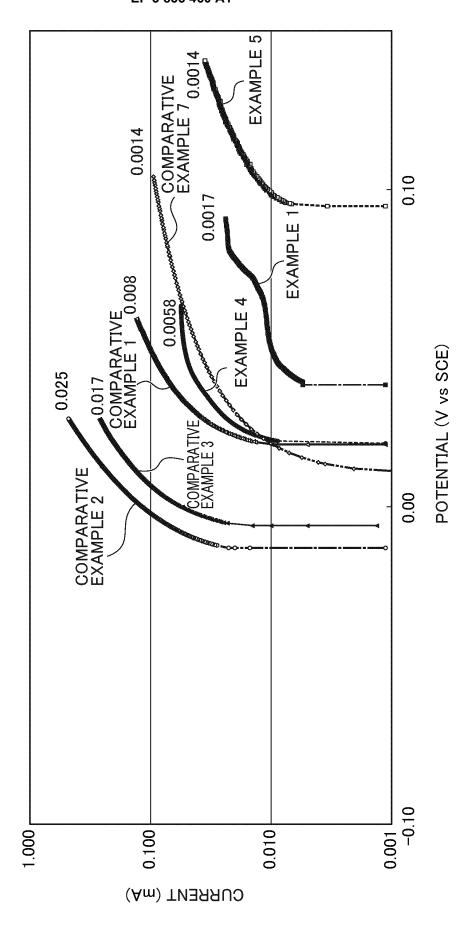




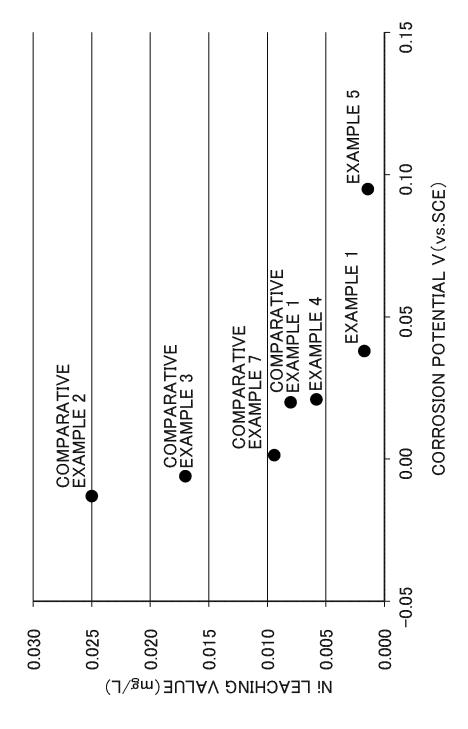












#### INTERNATIONAL SEARCH REPORT International application No. PCT/JP2019/020627 A. CLASSIFICATION OF SUBJECT MATTER 5 Int. Cl. C25D7/00(2006.01)i, C25D3/12(2006.01)i, E03C1/042(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED 10 Minimum documentation searched (classification system followed by classification symbols) Int. Cl. C25D7/00, C25D3/12, E03C1/042 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan Published unexamined utility model applications of Japan Registered utility model specifications of Japan Published registered utility model applications of Japan 15 1922-1996 1971-2019 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. JP 2015-212417 A (KIESOW DR. BRINKMANN GMBH & CO. 1, KG) 26 November 2015, paragraphs [0050]-[0098] & 25 EP 2937450 A1 & DE 102014207778 B & SI 2937450 T & PT 2937450 T & PL 2937450 T JP 2010-185116 A (NISSAN MOTOR CO., LTD.) 26 Α 1, 2 August 2010, paragraphs [0016]-[0028], [0045]-30 [0071] & US 2012/0052319 A1, paragraphs [0028]-[0040], [0057]-[0084] & WO 2010/092622 A1 & EP 2396455 A1 & CN 102317504 A & RU 2011137553 A 35 Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is 45 special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means combined with one or more other such documents, such combination being obvious to a person skilled in the art document published prior to the international filing date but later than document member of the same patent family the priority date claimed Date of the actual completion of the international search Date of mailing of the international search report 13.08.2019 50 05.08.2019 Authorized officer Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan Telephone No. 55 Form PCT/ISA/210 (second sheet) (January 2015)

#### INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/020627

5	C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT				
	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
10	A	JP 2006-316480 A (HAYAKAWA VALVE SEISAKUSHO KK) 24 November 2006, paragraphs [0025]-[0032], fig. 1 (Family: none)	1, 2		
15	Е, А	JP 6542437 B1 (OKUNO CHEMICAL INDUSTRIES CO., LTD.) 10 July 2019, paragraphs [0012]-[0052] (Family: none)	1, 2		
20					
25					
30					
35					
40					
45					
50					
55	E DOTAGA (A)	In (continuation of second sheet) (January 2015)			

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

#### 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

• JP 2015212417 A [0008]