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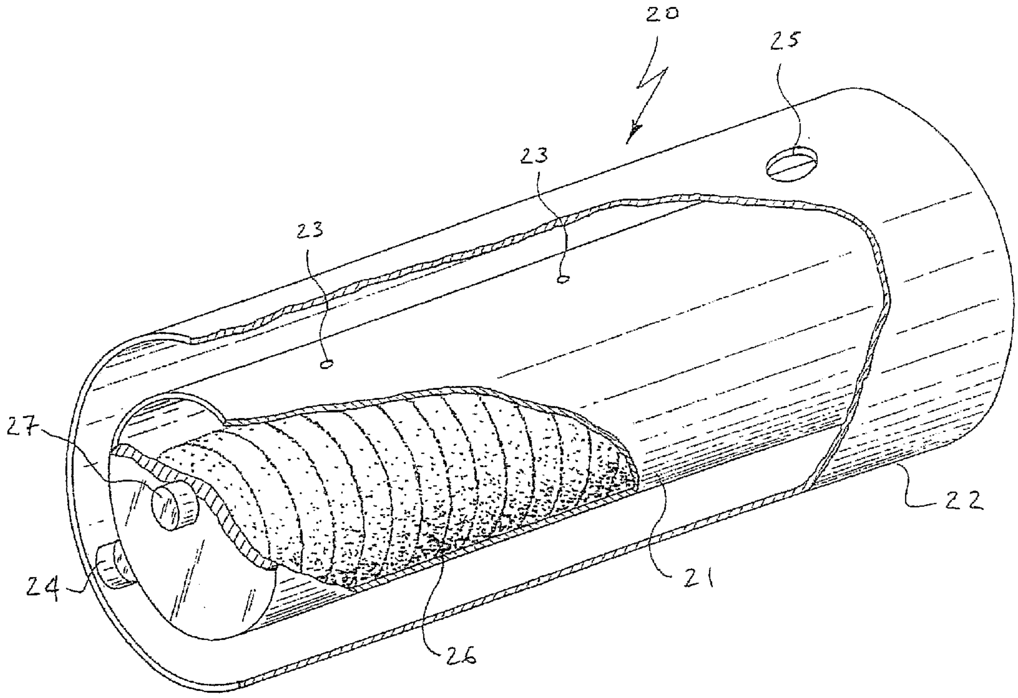
(54) Title: MIXTURES FOR EVAPORATION OF LITHIUM AND LITHIUM DISPENSERS



(57) Abstract: There is described the use of mixtures of lithium salts with reducing agents for lithium evaporation, particularly to be used in the manufacturing of electroluminescent organic displays. Lithium dispensers based on the use of these mixtures are also described.

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“MIXTURES FOR EVAPORATION OF LITHIUM AND LITHIUM DISPENSERS”

The present invention relates to mixtures to be employed for lithium evaporation in the industrial applications requiring the same, as well as to lithium dispensers using these mixtures.

Lithium is employed since long in the electronic field. In particular this metal has been used in the past for the production of photo-sensitive surfaces, such as of image intensifiers or photo-multiplying tubes. Another important use of lithium, in the form of alloys or salts, is in the formation of battery elements.

A new field of application of lithium is in the OLED (“Organic Light Emitting Display”) screens. Due to the importance of this application, in the following reference will be made in particular to this one, but the invention has a more general applicability.

In brief, an OLED is formed of a first planar transparent support (made of glass or plastics); a second support not necessarily transparent, that can be made in glass, metal or plastics, essentially planar and parallel to the first support and fixed along the perimeter thereof, so as to form a closed space; and an active structure for the image formation in said space. In its turn the active structure is formed of a first series of transparent, linear and mutually parallel electrodes, generally having anodic functionality, being deposited on the first support; deposited on the first series of electrodes, a multilayer of different electroluminescent organic materials, comprising at least one layer of a material conductor of electrons and one layer of a material conductor of electronic vacancies; a second series of linear and mutually parallel electrodes that are orthogonally oriented with respect to those of the first series and having cathodic functionality, being in contact with the opposite side of the multilayer of organic materials, so that the latter is comprised between the two series of electrodes. For a more detailed explanation of the structure and the operating principle of OLED screens reference can be made, for example, to patent applications EP-A-845924, EP-A-949696, JP-A-9-078058 and to patent US 6,013,384.

Recently it has been found that the addition of small quantities of electron-donor materials to the OLEDs structure allows reducing the difference of potential to be applied to the two series of electrodes for the functioning of the screens and therefore the energy consumption of these. In particular US patent 6,013,384 discloses the use of these metals for the doping of one or more layers of the organic multilayer, while US patent 6,255,774 discloses the formation of very thin layers (less than 5 nanometers) between the cathodes and the contiguous organic layer. As it is clear from reading these two patents (particularly from the examples), an element being especially suitable to this purpose is lithium, probably due to its small dimensions allowing the production of particularly thin, continuous layers or its dispersion in organic matrices.

Due to the high reactivity to the atmospheric gases and moisture, lithium (alike any alkali metal) generally is not industrially employed in the form of pure metal, but rather in form of compounds that are stable in air at room temperature. Most generally used compounds are the dichromate, $Li_2Cr_2O_7$, or more commonly the chromate Li_2CrO_4, in admixture with a reducing agent. By heating these mixtures at temperatures generally higher than 500 °C a reaction takes place by which chromium is reduced to a lower valence with the consequence of liberating lithium as a vapor. As reducing agents aluminum, silicon or getter alloys, i.e. titanium- or zirconium-based alloys with aluminum or one or more transition elements, are generally used. The use of these mixture is disclosed for example in patents US 2,117,735 and US 3,578,834. The mixtures are generally used at the inside of suitable dispensers capable of keeping solid particles, but having at least a portion of their surface permeable to the vapors of the alkali metal, such as shown e.g. in the patents US 3,579,459 and US 4,233,936.

However chromates and dichromates of alkali metals have the disadvantage of containing hexavalent chromium which can cause irritation by contact, swallowing or inhalation and can be carcinogenic in case of long exposures.

To avoid the use of chromium salts it has been proposed the utilization of lithium alloys, such as with aluminum. An example of the use of such alloys is given in the article “Simple source of Li metal for evaporators in ultrahigh vacuum (UHV) applications”, by F.J. Esposto et al, published on J. Vac. Sci. Technol., pages 3245-7, Vol. 12, no. 6 of 1994. Another example of a similar application is given in Japanese patent application publication JP 2004-164992. However employing these alloys is troublesome owing to their very irregular properties of lithium evaporation, with sudden emissions of metal, which make them essentially unusable in the industrial production.

International patent application publications WO 2004/066337 A1, WO 2004/066338 A1 and WO 2004/066339 A1 describe, respectively, the use of tungstates, molybdates and vanadates of alkali metals for the release of these latters, without however specifically describing or referring to lithium salts.

Object of the present invention is to provide mixtures for lithium evaporation which overcome the problems of the prior art.

Another object of the present invention is that of providing lithium dispensers employing these mixtures.

These and additional objects are achieved by means of the present invention dealing with mixtures between a lithium salt and a reducing agent, characterized in that the lithium salt is chosen among the titanate (Li_2TiO_3), tantalate ($LiTaO_3$), niobate ($LiNbO_3$), tungstate (Li_2WO_4) and zirconate (Li_2ZrO_3).

The invention will be described in the following with reference to the Figures, in which:

- Fig. 1 shows a perspective, partially cut-away section of a possible lithium dispenser according to the invention;
- Fig. 2 shows a perspective, partially cut-away section of a preferred form of lithium dispenser according to the invention; and
- Fig. 3 shows a graph referring to lithium evaporation properties of dispensers using the mixtures of the invention.

The inventors have found that mixtures of one or more reducing agents with a lithium salt chosen among the above-mentioned ones, not only eliminates the necessity of making recourse to compounds of hexavalent chromium, but have also additional properties that render advantageous their industrial utilization. Firstly the features (in particular the speed) of lithium evaporation can be easily controlled and reproduced. Furthermore the mentioned lithium salts are much less hygroscopic than the chromium salts, thus reducing the risk that during the lithium evaporation also moisture may evaporate, which is extremely dangerous for the OLED's functioning. Among the cited salts the preferred one is the titanate because it is the one showing the highest percentage content of lithium by weight and also because in the tests carried out by the inventors it has been found that this salt is the one requiring the slightest energy quantity for its evaporation; besides, it has been observed that lithium titanate gives rise to a particularly smooth lithium evaporation, that is thus easily controllable.

US patent 6,753,648 B2, in the name of the applicant, describes salts similar to those of the present invention, for the evaporation of cesium. However, owing to the difference of chemical characteristics between lithium and cesium (due to the particularly reduced dimensions and the high polarizability of the ion Li^+ with respect to Cs^+), the teachings of the cited US patent cannot be applied directly to the case of lithium; for example the molybdate anion forms with cesium a salt useful for evaporation of the alkali metal, whereas with lithium it forms a salt giving rise to sudden and uncontrollable evaporations, unsuitable in the industrial applications; on the contrary cesium titanate is useless in practice because it is excessively hydroscopic, whereas lithium titanate has turned out to be the preferable salt for lithium evaporation.

The reducing agent employed in the mixtures of the invention can be one of the already known components that are employed in the dispensers based on chromates, such as aluminum, silicon, zirconium or titanium, or alloys containing zirconium or titanium, such as the alloy of percent composition by weight Zr 84% - Al 16%, manufactured and sold by the applicant under the name St 101®, or the alloy having the weight composition Zr 76.5% - Fe 23.5%, manufactured and sold by the applicant with the name St 198®. It is also possible to use a mixture of a plurality of reducing agents.

In order to enhance the contact between the compound of lithium and the reducing agent, these are preferably employed in a powdered form. Both the mixture components have generally particle size of less than 1 mm and preferably lower than 500 μm; still more preferably the particle size is comprised between about 10 and 125 μm. Powders with particles having a size of less than 10 μm are generally difficult to be treated in manufacturing and to be kept inside the dispenser; furthermore, in case of the reducing agent, excessively fine powders can become pyrophoric giving rise to safety problems in the manufacturing plant. On the contrary, with powders with particle size greater than those indicated the contact between the two components of the mixtures becomes worse and the reaction leading to lithium evaporation results to slow down.

The weight ratio between the lithium salt and the reducing agent can vary within wide limits. Preferably such a ratio is comprised between 10:1 and 1:10. The use of the lithium salt in great excess with respect to the reducing agent offers no practical advantage; vice versa, especially when the reducing agent is a getter alloy such as the cited St 101® alloy, an excess thereof in the mixture can be useful because the portion not involved in the reaction with the lithium salt can have the effect of sorbing the gases that may be liberated during the reaction. A preferred weight ratio between the lithium salt and the reducing agent is 1:5.

The mixture can be used in the form of loose powders. Preferably, however, it is used in the form of pellets, having the advantage of further improving the contact between the mixture components and facilitating the operations of loading the container. Another advantage of pellets as compared to powders, that has been observed by the inventors, is that pellets require a lesser amount of energy for lithium evaporation, and lithium load of the mixture is used more thoroughly, as described in greater detail by a test in the examples section.

The container can be made in any material and shape compatible with the application.

In particular, as far as the material is concerned, this should be chemically inert against the processing atmosphere and the lithium dispensing mixture at any temperature foreseen in use, which can exceed 1000 °C; furthermore, at the temperatures of use, the material forming the container should not undergo substantial physical alterations such as to modify either its mechanical strength or shape, and must show as low as possible values of gas emission. Materials having these features are for example metals or metallic alloys, a few ceramics or graphite. Employing metals and alloys is preferred due to their easier workability and formability. Another advantage in the use of metals and alloys is that the dispenser can be heated at the temperature of lithium evaporation simply by flowing current through the container walls. Preferred metals and alloys for making the container are molybdenum, tantalum, tungsten, nickel, steel and nickel-chromium or nickel-chromium-iron alloys.

The shape of the container can be any whatsoever among those known from patents US 3,578,834, US 3,579,459, US 3,598,384, US 3,636,302, US 3,663,121, US 4,233,936 and US 6,753,648 B2. Containers of various shapes and materials are also available in the trade, for instance by the Austrian company Plansee or the US company

Midwest Tungsten Service. A first possible shape of dispenser of the invention is shown in figure 1. The dispenser 10 consists of a container with a mixture of the invention inside. The container is formed by the assembly of an upper part 11 and a lower part 12; the two parts are preferably made of metal, and joined to each other e.g. by spot-welding. The lower part shows in its central zone a recess (obtained e.g. by cold stamping), having housed therein a mixture of the invention, while the upper part has a number of openings 13, 13', ..., to allow the emission of lithium vapors; in the drawing the area of part 11 defined by dashed lines corresponds to the recess in part 12. The mixture of the invention can be present in the recess of part 12 in powder form as shown in the drawing, wherein the mixtures is illustrated as element 14; in alternative it is possible to form pellets of mixture and fill therewith the recess. Dispenser 10 has at its two ends "wings" 15 and 15', which are particularly adapted for the connection with electrical terminals for heating the dispenser by direct current flow.

Another possible shape of dispenser is shown in figure 2. This container is the object of, and is described in greater detail in, Italian patent application No. MI2004A002279. The dispenser, 20, is formed of a central container 21 and a shield 22. Container 21 is closed apart from openings 23; in the drawing it is represented the case that the container has three openings, one of which is hidden by the shield, but these could be present in any number. Shield 22 is concentrically arranged around container 21, and kept in the correct position by spacers 24 (only one shown); the shield has openings 25 at positions radially corresponding to openings 23. In the container is present the mixture of the invention between a lithium salt and a reducing agent; the mixture is represented in this case as a plurality of pellets 26, laid in the bottom of the container one aside another. Evaporation of lithium is caused by heating the container, for instance by feeding current to the ends thereof through contacts 27 (only one shown).

The invention will be further illustrated by the following examples.

EXAMPLE 1

A container like the one shown in figure 1 is manufactured by employing sheets of Inconel (an alloy mainly comprising nickel-chromium, plus minor amounts of other metals) having a thickness of 0.2 mm. The container has lateral dimensions of 100 x 24 mm, with a recess 6 mm high being filled up with about 10 g of a mixture between the cited alloy St 101 and Li_2TiO_3 in a weight ratio of 5:1; the mixture is employed in the form of pellets having diameter of 6 mm and height of 3 mm, being obtained by compression of the powders mixture under a pressure of about 1700 Kg.

The dispenser is placed on the bottom of an evacuated chamber; a small glass plate, of lateral dimensions 3 x 3 cm is placed above the dispenser at a distance of about 20 cm. At the ends of the container ("wings" 15, 15' in Fig. 1) is applied a direct current of 100 A during about six hours; the current flow heats the dispenser up to a temperature of about 800 °C, thus causing the reaction between the mixture components and lithium evaporation; a fraction of the evaporated lithium condenses on the glass plate forming a thin film thereon.

During the test the chamber is connected to a sample line of a mass spectrometer for monitoring the quantities of emitted gases during the evaporation (obviously except for lithium; due to condensation onto the cold walls of the chamber, this element is not sent to the MS measurement); no substantial gas emissions are observed during the whole test.

At the end of the test the quantity of evaporated lithium is estimated by measuring the weight difference of the dispenser before and after the test; by taking into account the results of the in-line MS measurement, the weight difference is completely ascribed to the lithium evaporation, thus resulting in a metal evaporation of 100%.

An analysis of the film formed on the glass plate is also carried out to check its purity, by dissolving it in a HCl solution and chemically analyzing the thus obtained solution through atomic absorption; the film contains a quantity of impurities lower than 1% by weight.

In the chamber, near the glass plate there is also mounted a quartz crystal monitor (QCM), a device well known in the field to measure the growing speed of thin films by exploiting the variation of the quartz crystal vibration frequency in function of the weight of material deposited thereon; from the knowledge of density and acoustic impedance of metallic lithium, the weight increase is referred to the increase of film thickness with time, thus obtaining a constant speed of film deposition with a value of about 0.2 Ångstrom per second (Å/s).

EXAMPLE 2

It is prepared a lithium dispenser like the one shown in figure 2, comprising a cylindrical central container and a shield both made of stainless steel of thickness 0.2 mm. The container is 10 cm long and has a diameter of 3.1 cm, with two holes of diameter 2.5 mm spaced apart 5 cm along a line on its upper part; the shield, concentrically arranged around the container, is as long as this latter and has a diameter of 3.4 cm, with four holes of diameter 11 mm, two holes facing the holes in the container surface, and the other two ones placed between the first two ones and spaced apart 12 mm from each other. The container is filled with 110 g of a mixture between the cited alloy St 101 and Li_2TiO_3 in a weight ratio of 1:1; the mixture is employed in the form of loose powders.

The dispenser is placed on the bottom of an evacuated chamber and heated by feeding direct current to the ends of the central container, thus causing lithium evaporation; the test lasts about 40 hours. In the chamber is present a QCM at a distance of 36 cm from the dispenser to measure the speed of growth of a lithium film, that's proportional to the rate of evaporation of the same metal from the dispenser. The QCM is connected via a feed-back loop to the power source, and the system is regulated to obtain a growth speed of 0.28 Å/s. As evaporation proceeds, the amount of lithium left in the dispenser gets lower, and the temperature required to keep the rate of evaporation increases; this implies a request for higher power, and thus a higher value of current, with time, up to a maximum current value of 300 A (the limit value the system can supply).

In figure 3 are reported the results of this test: curve 1 represents the trend of film deposition rate (FDR, measured in Å/s, on the left-hand axis of the graph) as a function of the thickness of lithium film deposited (T, measured in Å); curve 2 represents the trend of the voltage measured at the ends of the dispenser during the test (Volts, V, right-hand axis of the graph).

EXAMPLE 3

The test of example 2 is repeated, with the only difference that in this case the lithium dispensing mixture is present in the form of x pellets having diameter of 6 mm and height of 3 mm, each one of weight about 0.3 g, obtained by compression of the powders mixture under a pressure of about 1700 Kg.

The results of this test are reported in figure 3; curve 3 represents the trend of evaporation rate, while curve 4 represents the trend of the voltage measured at the ends of the dispenser during the test. Curve 2 is essentially superimposed to curve 1 all along the test, apart from the end tail where a difference in the behavior of dispensers charged with powders or pellets is observed.

As observed in the tests of example (in particular example 1), the mixtures of the invention are suitable for the use in industrial processes, as they show constant features of metal evaporation without sudden phenomena, do not give rise to substantial emissions of potentially harmful gases (such as e.g. water), and allow to grow lithium thin films of high purity in a reproducible way and with a constant speed. The comparison of results obtained in examples 2 and 3 shows that, while both powders and pellets are suitable for the purposes of the dispensers of the invention, dispensers charged with pellets may be preferable as these allow to evaporate lithium for a longer time with constant evaporation rate (up to a film thickness of about 25800 Å, curve 3 in fig. 3, vs. a thickness of about 22350 Å obtained with powders, curve 1 in fig. 3). The reason for this behavior has not been fully clarified yet, but it is believed that, at the operative temperatures for lithium evaporation, loose powders have a better surface contact than pellets and thus behave as better electrical conductors; as a consequence, when electricity flows across powders, less heat is generated compared to pellets, with the overall effect that using powders a higher current is required to heat the mixture to the temperature values effective to cause lithium evaporation. This interpretation seems to be confirmed by the two curves (3 and 4) in fig. 3, showing a high voltage drop at the ends of the dispenser charged with pills as compared to the one charged with loose powders, throughout the test.

CLAIMS

1. Mixture for lithium evaporation, comprised of a lithium salt and a reducing agent, characterized by the fact that the lithium salt is chosen among titanate (Li_2TiO_3), tantalate ($LiTaO_3$), niobate ($LiNbO_3$), tungstate (Li_2WO_4) and zirconate (Li_2ZrO_3).

2. Mixture according to claim 1, wherein the reducing agent is chosen among aluminum, silicon, zirconium, titanium or an alloy of zirconium or titanium.

3. Mixture according to claim 2, wherein said alloy is chosen between the alloy of weight percent composition Zr 84% - Al 16% and the alloy of weight percent composition Zr 76.5% - Fe23,5%.

4. Mixture according to claim 1, wherein said lithium salt and said reducing agent are in powder form.

5. Mixture according to claim 4, wherein said powders have particle size of less than 1 mm.

6. Mixture according to claim 5, wherein said powders have particle size of less than 500 μm.

7. Mixture according to claim 6, wherein said powders have particle size comprised between 10 and 125 μm.

8. Mixture according to claim 1, wherein the weight ratio between the lithium salt and the reducing agent is comprised between 10:1 and 1:10.

9. Mixture according to claim 8, wherein said weight ratio is 1:5.

10. Mixture according to claim 4, wherein said mixture of powders is compressed to form pellets.

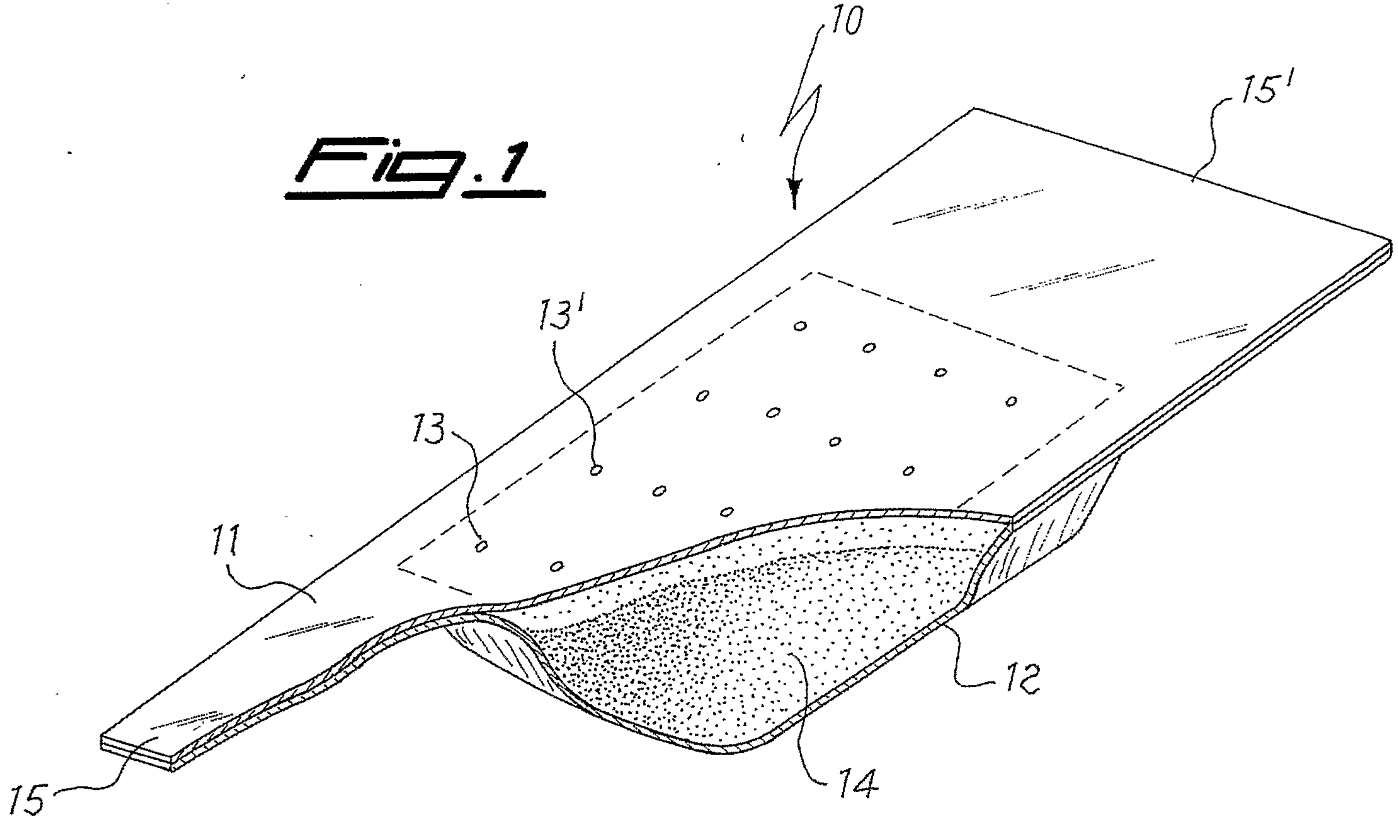
11. Lithium dispenser (10; 20) containing a mixture of claim 1.

12. Dispenser according to claim 11, formed as a metallic container provided with at least one opening (13, 13'; 23, 25) for the emission of lithium vapors.

13. Dispenser according to claim 11, wherein said container is made of a material chosen among metals, metallic alloys, ceramics and graphite.

14. Dispenser according to claim 13, wherein said container is made of a material chosen among molybdenum, tantalum, tungsten, nickel, steel or either nickel-chromium or nickel-chromium-iron alloys.

Fig.1



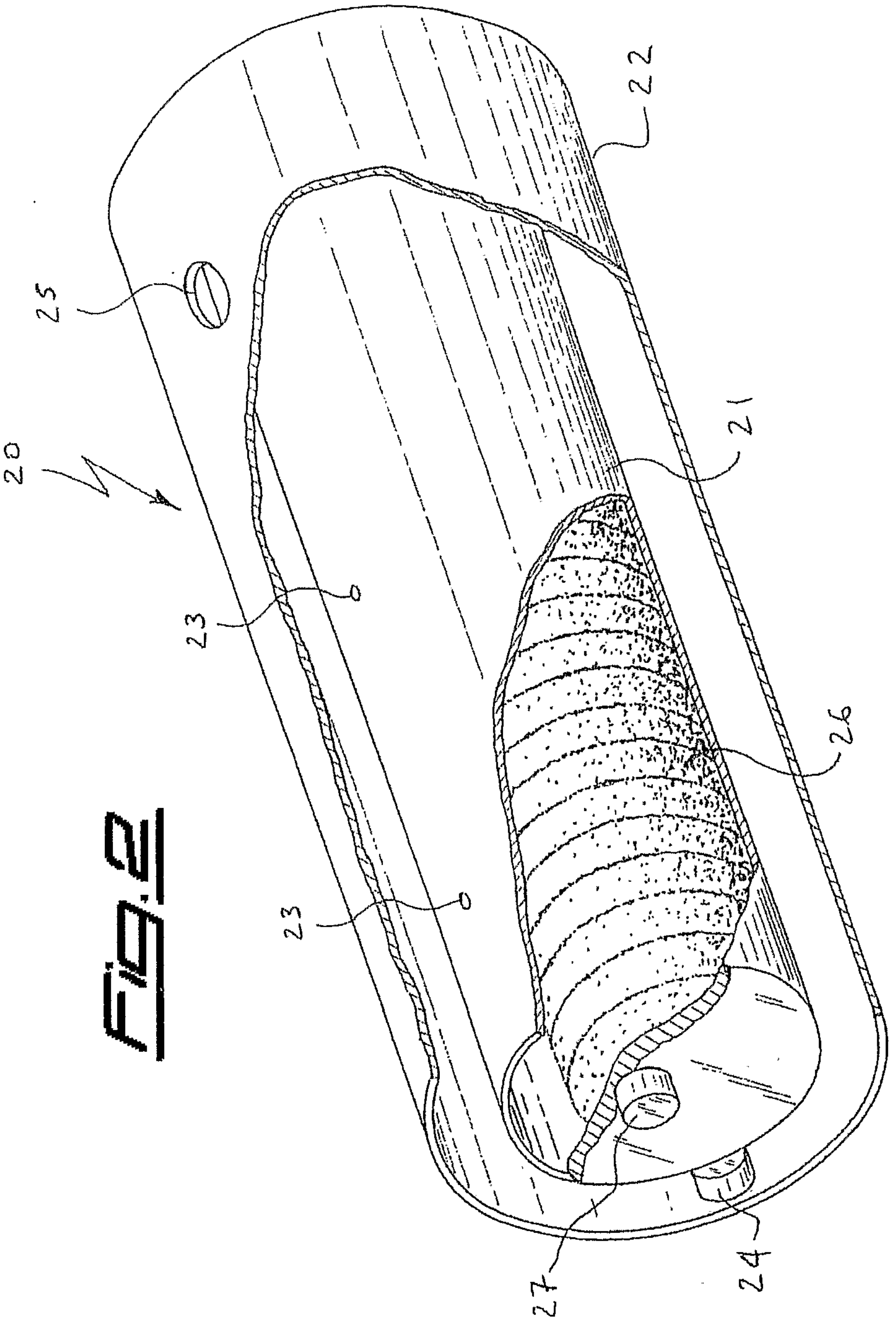
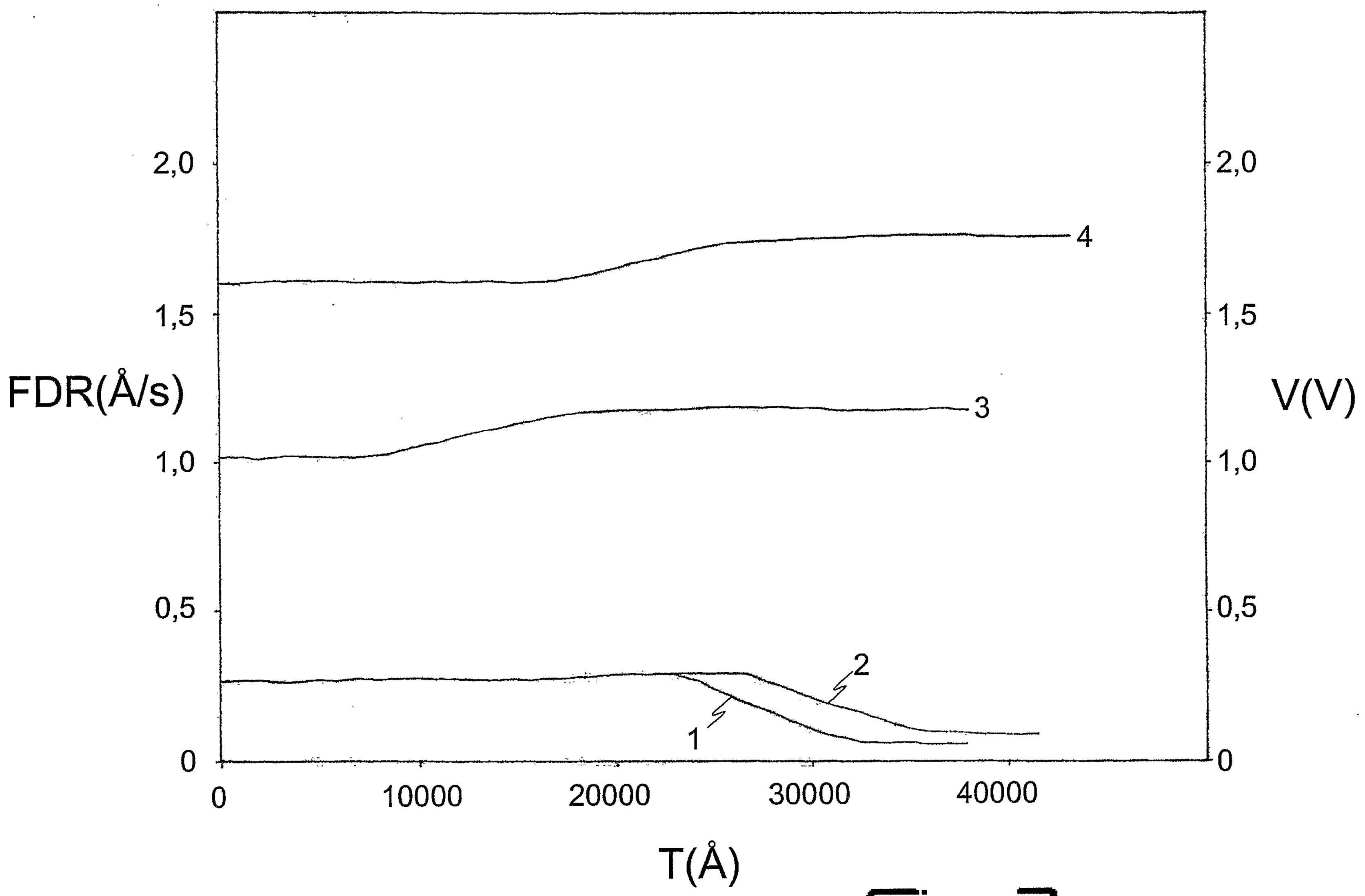


Fig.2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2
1
0
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30000
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T(Å)

Fig.3