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3,223,609

HYGROMETER

Filed Oct. 30, 1961

3 Sheets-Sheet 1

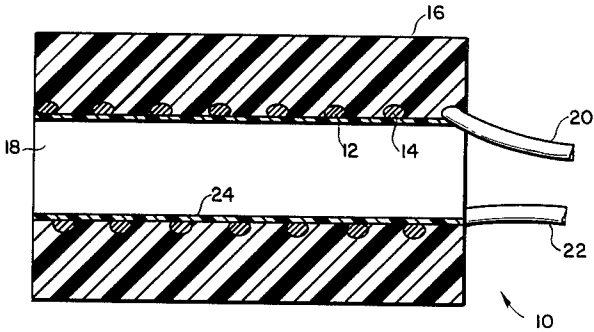


FIG. 1

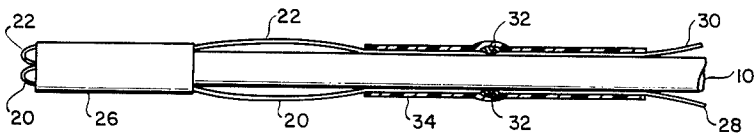


FIG. 2

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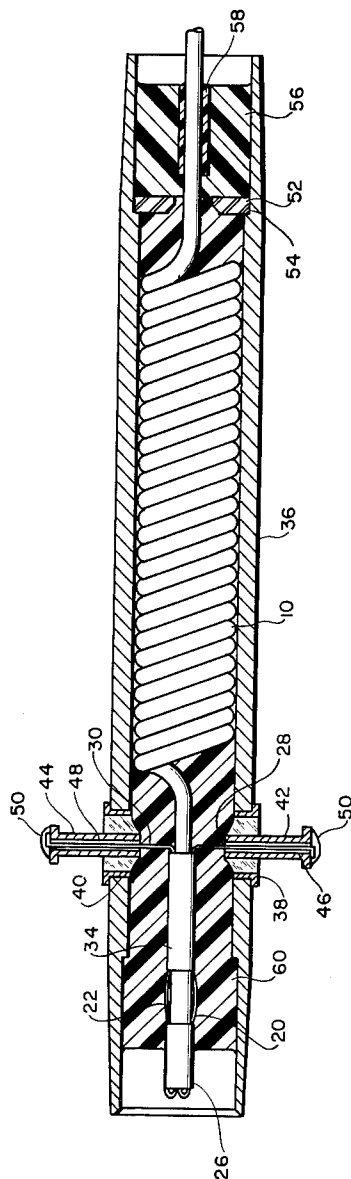


FIG. 3

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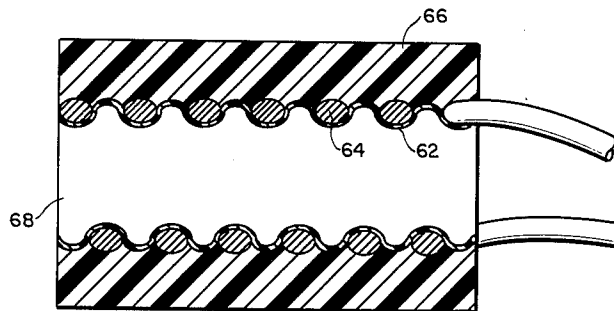


FIG. 4

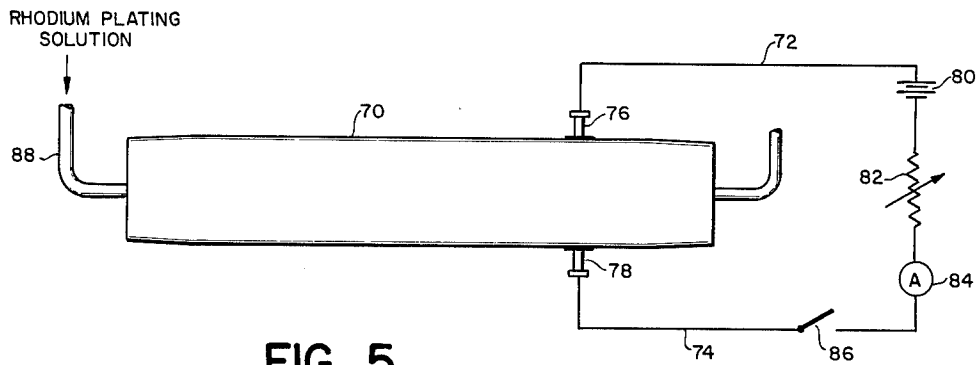


FIG. 5

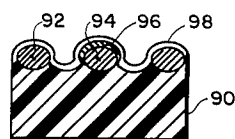


FIG. 6

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HYGROMETER

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9 Claims. (Cl. 204-195)

This invention relates to hygrometers and more particularly relates to an improved electrolytic hygrometer cell.

Electrolytic hygrometers have been widely used for determining the moisture content of fluid streams in industrial processes in which the presence of even minute percentages of moisture is of great significance. This type of hygrometer has numerous advantages over other moisture determining devices, particularly when used in conjunction with continuous process streams, as it is quite selective to water, has a rapid speed of response, and is completely quantitative over wide ranges of moisture concentration, thereby eliminating the need for frequent calibration and standard samples.

Electrolytic hygrometers depend for their operation on the relationship between the amount of water present in a hygroscopic substance and the amount of current necessary to electrolyze it. The active elements of the most commonly available hygrometers comprise a pair of helical platinum conductors partially embedded in a supporting tubular jacket, the interior of which is coated with a hygroscopic substance which bridges the spaces between adjacent turns of the helices. The gas or vapor to be tested is passed over the hygroscopic substance which absorbs the moisture present in the gas or vapor and becomes conductive. An electric current is then passed between the adjacent turns of the two platinum conductors and the water is electrolyzed to hydrogen and oxygen. The amount of current necessary to completely electrolyze the water is, of course, a measure of the moisture content of the fluid being tested.

Although the cells described are satisfactory for most applications, their useful life is short, averaging only about 40,000 part per million-hours when used at a sample flow rate of 100 cubic centimeters/minute. Thus, in a process stream in which the moisture content is 1,000 parts per million, the average cell will fail in 40 hours. This short lifetime results in great inconvenience in all applications, and in those applications where it is desired to continuously monitor a process stream whose moisture content is highly critical, that is, in the very applications wherein the cells are most effective, the usefulness of the electrolytic hygrometer is severely limited.

It has been noted that after a period of use a black deposit, apparently platinum or a platinum compound, appears between the platinum electrodes. The formation of this deposit occurs most rapidly at the entrance and exit portions of the cell, but takes place to some degree throughout its entire length. The deposit eventually builds up to a point where it forms a metallic bridge between adjacent turns of the electrodes and being electrically conductive, causes a short circuit between them, resulting in cell failure.

It has also been found that the presently available cells must be modified for use with gas streams comprising more than 50 percent hydrogen and that even when modified, cell accuracy is extremely sensitive to changes in gas condition. It is believed that the inaccuracy of the cell when used with a hydrogen stream is due primarily to recombination of the oxygen liberated by the electrolysis with the hydrogen stream, thus creating additional water which is again electrolyzed, possibly several times. The recombination of hydrogen and oxygen is apparently catalyzed by the presence of platinum or platinum compounds in the cell, both the electrodes themselves and the de-

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posits between them having an effect on the rate of recombination.

According to the present invention, it has now been found that an electrolytic hygrometer cell may be provided that has an extremely long life expectancy and which may be used with equal facility on streams containing any percentage of hydrogen. The important advantage of long life expectancy may be obtained by providing the cell with at least one rhodium electrode which serves as the anode when the cell is operatively connected in an appropriate electrical circuit. For use on hydrogen streams, the anode should be rhodium and the cathode should be a conductor which does not catalyze the recombination of hydrogen and oxygen. Both electrodes may be rhodium for this application.

It is therefore a primary object of the present invention to provide an electrolytic hygrometer cell which has a life expectancy far in excess of any cell heretofore known.

It is another object of the present invention to provide an electrolytic hygrometer cell which may be used on a fluid stream regardless of its hydrogen content.

It is a further object of the present invention to provide an electrolytic hygrometer cell whose active element has at least one rhodium electrode.

It is a still further object of the present invention to provide a rhodium electrode for an electrolytic hygrometer cell.

These and further objects and advantages of the invention will become more apparent upon reference to the following specification and claims and appended drawings wherein:

FIG. 1 is a sectional view of one type of active element of an electrolytic hygrometer cell incorporating the teachings of the present invention;

FIG. 2 is a view partly in section of a portion of an electrolytic hygrometer cell according to the present invention;

FIG. 3 is a view partly in section of an electrolytic hygrometer cell according to the present invention;

FIG. 4 is a sectional view of another form of active element of an electrolytic hygrometer cell incorporating the teachings of the present invention;

FIG. 5 is a schematic showing of an electrical circuit used to form an electrolytic hygrometer cell in accordance with one aspect of the present invention; and

FIG. 6 is a sectional view of a portion of another form of active element of an electrolytic hygrometer cell incorporating the teachings of the present invention.

Referring now to FIG. 1, there is shown for use in electrolytic hygrometers an active element, generally indicated at 10, which comprises a pair of helically wound, substantially pure rhodium electrodes 12 and 14 partially embedded in a jacket 16 of a suitable insulating material, for example, a thermoplastic resin such as polychlorotrifluoroethylene. If desired, this jacket may be constructed of glass or another suitable material. The unembedded or active portions of the rhodium electrodes 12 and 14 make up a portion of the surface of an interior annular passageway 18 extending through the thermoplastic jacket 16. The electrodes 12 and 14 terminate in a pair of conductors 20 and 22 which protrude outwardly from the end of the thermoplastic jacket 16 so that the electrodes may be connected into a suitable electrical circuit. The annular surface of the interior passageway 18 through the jacket 16 is coated with a thin film of a suitable hygroscopic substance, for example, phosphorus pentoxide, so that each segment of insulating material separating alternate active portions of the rhodium electrodes 12 and 14 is bridged by a material which may become conductive.

The active element just described is preferably made in accordance with the teachings of U.S. application

Serial No. 134,506, filed August 28, 1961, by Douglas B. Gardner and assigned to the assignee of the present application. Briefly, this element is made by space-winding the electrodes 12 and 14 on a stainless steel mandrel, extruding the jacket 16 over the mandrel and the electrodes, removing the mandrel, peeling the jacket back to expose the ends of the electrodes, and passing a slurry of phosphoric acid through the annular passageway previously occupied by the mandrel to form the bridging film of phosphorus pentoxide.

The use of rhodium as the electrode material vastly extends the useful life of an electrolytic cell. Tests indicate that the life expectancy of an electrolytic cell utilizing rhodium electrodes is well over 500,000 part per million-hours in contrast with the aforementioned 40,000 part per million-hours for cells utilizing platinum electrodes. It has been found that when substantially pure rhodium electrodes are used, the inter-electrode deposits previously referred to are completely or nearly completely eliminated.

It has also been discovered that the incorporation of rhodium electrodes into an electrolytic cell enables it to be used to accurately measure the moisture content of gas or vapor streams, regardless of their hydrogen content. The rhodium electrodes themselves do not appear to catalyze the recombination of liberated oxygen and hydrogen as do platinum electrodes when they are employed in a similar environment and, moreover, no inter-electrode deposits are formed which might act as a catalyst for this reaction. As a result, the recombination, if any, that takes place is insignificant, and the only water electrolyzed is that which enters the cell in the gas or vapor stream.

In order to improve cell performance markedly, the electrodes need not be of substantially pure rhodium but may be composed of an alloy of rhodium. These alloys, however, do not extend the life of a cell as greatly as does substantially pure rhodium. For example, an alloy of 60 percent platinum and 40 percent rhodium was found to increase the life of a cell by approximately a factor of 10 over a cell having platinum electrodes. This example is, of course, strictly illustrative, as any alloy having a rhodium content not substantially less than 40 percent will be useful, for example, alloys of rhodium and iridium or osmium as well as other alloys of platinum and rhodium will appreciably increase cell life.

Furthermore, it has been found that only the electrode which serves as the anode in the electrolysis need be of rhodium to prevent the deposition of inter-electrode deposits. The use of a pair of rhodium electrodes is, however, preferred because the use of a single electrode requires that one terminal of the cell be always positive, thus decreasing its convenience and adaptability in use. In addition, the presence of the platinum electrode would somewhat increase the recombination rate of liberated oxygen and hydrogen if the cell were used on a hydrogen stream, thus making it less attractive for this use. The presence of platinum in a rhodium-platinum alloy would also have this effect on a hydrogen stream.

Referring now to FIGS. 2 and 3, there is shown a complete electrolytic cell incorporating an active element similar to that shown in FIG. 1. As may be seen in FIG. 2, the conductors 20 and 22 protrude from the end of the element 10 and are bent back over the jacket at an angle of 180° and held snugly against the jacket by means of a sleeve 26, preferably of polytetrafluoroethylene. The extremities of the rhodium conductors 20 and 22 are joined to a pair of copper conductors 28 and 30, in any suitable fashion, for example, by means of solder 32. This junction is protected by a thermofitting plastic tube 34 which, together with the polytetrafluoroethylene sleeve 26, prevents movement of the somewhat delicate rhodium conductors 20 and 22 and thereby protects them from being broken during the assembly and use of the cell.

The complete cell is assembled as shown in FIG. 3.

In the construction of this cell, a suitable length of active element 10 is coiled in any desired manner, for instance, it may be heated and wrapped around a mandrel of suitable diameter. When the element cools, it will remain in the shape of a helix and may be easily introduced into a stainless steel casing 36. The casing 36 is provided with a pair of ports 38 and 40 which are sealed by a pair of insulating members 42 and 44 made of any suitable material. As shown, these members take the form of commercial metal to glass hermetic feed-through terminals. The insulators 42 and 44 are provided with annular passageways 46 and 48 for the passage of conductors 28 and 30 therethrough from the active element in the interior of the casing 36 to the point where they may be connected into an appropriate indicating circuit. After the conductors 28 and 30 have been drawn through the passageways 46 and 48, these passageways are sealed closed by any suitable means, for example by solder 50.

After the active element 10 has been inserted into the casing 36 and the conductors 28 and 30 drawn through the insulating members 42 and 44, one end of the casing 36 is closed by means of a steel washer 52 that rests upon a shoulder 54 provided on the inner surface of the casing 36. A polytetrafluoroethylene plug 56 having a slightly tapered interior passageway is then inserted into the end and seated on the washer 52 and the seal is then completed by passing a polytetrafluoroethylene sleeve 58 over the end of the active element 10 and forcing it against the taper of the passageway in the plug 56 until it is firmly seated. The interior of the casing 36 is then filled with a suitable potting compound 60, care being taken that none of the potting compound blocks the open end of the element 10. The resulting structure is a durable, long-lasting electrolytic hygrometer cell that can be used with equal effect on streams having high or low hydrogen contents.

Referring now to FIG. 4 there is shown another type of active element that may incorporate the teachings of the present invention. This type element is made by wrapping a pair of rhodium electrodes separated by a pair of copper spacer windings around a mandrel and extruding a suitable jacket e.g., of polytetrafluoroethylene over the wires and the mandrel. The mandrel is then removed and the copper spacer windings etched away. The surface of the annular passageway formed by the removal of the mandrel is then coated with a thin film of a suitable hygroscopic substance. This type element can be incorporated into the cells shown in FIG. 3 in place of the element 10. The use of rhodium in place of platinum for the electrodes in this type of cell element also increases its life in the same fashion as previously described.

Since it is only necessary that the active portions of the anode electrode be of rhodium, long-lasting cells may be produced by plating the active or unembedded portions of one or both platinum electrodes with a film of rhodium. A circuit suitable for such a process is shown in FIG. 5. In this figure, a suitable cell 70 is shown from which extends a pair of conductors 72 and 74 through a pair of insulating members 76 and 78. The active element of the cell in this figure is constructed with platinum electrodes and may be formed in the manner shown in FIGS. 1 or 4 or in any other suitable fashion.

The conductors 72 and 74 are connected in a series circuit with a suitable source of voltage 80, a variable resistor 82, an ammeter 84, and a switch 86. A commercial rhodium plating solution is then introduced into the active element through a conduit 88 and the switch 86 closed. The resulting voltage across the two cell electrodes causes the electrode connected as the cathode to be plated with rhodium. The cell element is then rinsed and filled with phosphoric acid solution in the usual manner.

FIG. 6 shows a portion of an active element produced by the process of FIG. 5. The active element used in the plating process was one similar to that shown in FIG. 4. The active elements comprise a suitable jacket 90 in

which are embedded a pair of platinum electrodes 92 and 94. After the electroplating, a film of rhodium, shown in greatly exaggerated fashion at 96, covers the active or exposed, portions of the electrode 94. These exposed portions are the only electrically active portions of the electrodes, as the remaining portions of the electrodes are completely embedded in insulating material. After the rhodium is plated onto the active portion of the electrode 94, a film of a hygroscopic substance 98 is coated on the entire surface, as described previously. When this cell is operated with the positive electrolyzing voltage applied to the rhodium plated electrode, the cell has an extremely long life compared with any presently known. Cells made in this fashion, however, have the same disadvantages as previously mentioned for cells having only one rhodium electrode.

From the foregoing, it can be seen that an electrolytic hygrometer cell is provided that is far more useful and long-lasting than any others heretofore proposed. These salutary results are achieved by using at least one electrode having an active surface containing rhodium. This rhodium-containing surface can be obtained by making either or both of the electrodes of substantially pure rhodium, an alloy containing rhodium, or by plating rhodium on the active surface of a platinum electrode.

The invention may be embodied in other specific forms not departing from the spirit or essential characteristics thereof, other forms of electrolytic hygrometer cells being equally improved by the use of the present invention as those described herein. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

I claim:

1. An electrolytic hygrometer cell having at least one electrode composed of rhodium.

2. An electrolytic hygrometer cell having at least one electrode whose active portion contains rhodium.

3. An electrolytic hygrometer cell having at least one electrode consisting of substantially pure rhodium.

4. An electrolytic hygrometer cell having a pair of spaced electrodes, said electrodes consisting of substantially pure rhodium.

5. In an electrolytic hygrometer, the improvement of providing at least one electrode with an active portion containing rhodium.

6. An electrolytic hygrometer capable of operation in a hydrogen atmosphere without substantial hydrogen recombination comprising: an inner jacket of insulating material having a passage therethrough; a pair of spaced electrodes supported in said jacket and having at least a portion thereof adjoining said passage; a hygroscopic

substance bridging the space between said electrodes; means to apply a potential between said electrodes; at least one of said electrodes being composed of rhodium.

7. An electrolytic hygrometer capable of operation in a hydrogen atmosphere without substantial hydrogen recombination comprising: an inner jacket of insulating material having a passage therethrough; a pair of spaced electrodes supported in said jacket and having at least a portion thereof adjoining said passage; a hygroscopic substance bridging the space between said electrodes; means to apply a potential between said electrodes; at least one of said electrodes having an active portion composed of rhodium.

8. An electrolytic hygrometer capable of operation in a hydrogen atmosphere without substantial hydrogen recombination comprising: an inner jacket of insulating material having a passage therethrough; a pair of spaced electrodes supported in said jacket and having at least a portion thereof adjoining said passage; a hygroscopic substance bridging the space between said electrodes; means to apply a potential between said electrodes; said electrodes composed of rhodium.

9. An electrolytic hygrometer capable of operation in a hydrogen atmosphere without substantial hydrogen recombination comprising: an inner jacket of insulating material having a passage therethrough; a pair of spaced electrodes supported in said jacket and having at least a portion thereof adjoining said passage; a hygroscopic substance bridging the space between said electrodes; means to apply a potential between said electrodes; said electrodes consisting of substantially pure rhodium.

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