Dec. 28, 1971 F. B. KUFFER 3,630,875

ELECTROLYTIC CELL HYGROMETER

Filed March 10, 1970

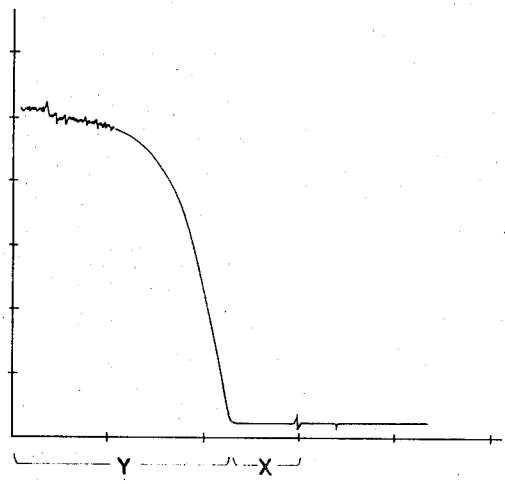


FIG. 1

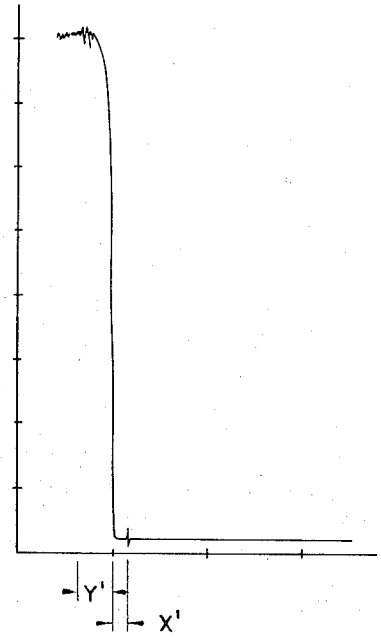


FIG. 2

INVENTOR.
FERNAND B. KUFFER
BY William F. McDonald
ATTORNEY

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HYGROMETER ELECTROLYTIC CELL

Fernand B. Kuffer, Brea, Calif., assignor to Beckman Instruments, Inc.

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U.S. Cl. 204—195 15 Claims

ABSTRACT OF THE DISCLOSURE

An hygrometer electrolytic cell having as an electrolyte an anhydride formed from an acid of an element selected from the group consisting of aluminum, boron, Group IV–A elements and Group V–A elements. The acid has blocked polymerization sites and contains not more than the equivalent of 19 carbon atoms.

BACKGROUND OF THE INVENTION

The instant invention relates to electrolytic cells and more specifically to electrolytic hygrometer cells. It is particularly applicable to the type hygrometer cell described in U.S. Pat. No. 2,830,945, and commonly known as a Keidel cell.

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

Electrolytic hygrometers of the Keidel type 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 generally comprise a pair of electrode wires, for example of platinum, or rhodium, frequently partially embedded in a supporting tubular jacket. The inter-electrode space is coated with a hygroscopic substance such as phosphoric acid which, when dried, becomes metaphosphoric acid, HPO_3. 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 electrolytic current is then passed between the two 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.

The normal response time for a cell of the type generally described above for a change in moisture level from near 0% humidity to near 100% relative humidity is about 10+ minutes for a properly operating cell. Frequently it would be desired to have a faster response time. An example of when a faster response time would be desired is if the hygrometer electrolytic cell were being used to provide data for the control of a process. Knowing how much water vapor was in the process stream ten minutes ago simply is not good enough. A more rapid response time is desired. Another example is the measurement of very low water concentrations, e.g. below 50 parts per million.

SUMMARY OF THE INVENTION

It is an object of the instant invention to provide an electrolytic cell having an electrolyte which will result in a much faster response time in the cell from changes in water concentration in the gas or fluid sample stream. The electrolyte advantageously is closely related to the conventional electrolyte and introduces no new factors for consideration in operating the Keidel cell.

According to the instant invention, the electrolytic cell has as an electrolyte an anhydride formed from an acid of an element selected from the group consisting of aluminum, boron, Group IV–A elements, and Group V–A elements. The acid has blocked polymerization sites and contains not more than the equivalent of 19 carbon atoms.

This description of the invention and the advantages thereof will become more apparent from the following detailed description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical presentation of an electrolytic cell employing a conventional electrolyte.

FIG. 2 is a graphical presentation of the response time of a cell similar to that of FIG. 1, but employing an electrolyte according to the instant invention.

DETAILED DESCRIPTION

A general description of the operation of an electrolytic cell of the Keidel type may be found above. The principal limitation on response time of the cell seems to be the chemical reactions involved. The reactions are commonly stated as follows:

$$2H_2O \xrightarrow{e^-} 2H_2 + O_2 \quad \text{(i)}$$

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \quad \text{(ii)}$$

$$2H_3PO_4 \xrightarrow{e} 3H_2O + P_2O_5 \quad \text{(iii)}$$

These reactions are idealized reactions and do not describe what actually occurs under the operating conditions of the cell. The last two reactions under the conditions of the cell may be more accurately represented as:

$$HPO_3 + H_2O \rightleftarrows H_3PO_4 \quad \text{(iv)}$$

The reverse reaction is asymptotic to HPO_3. The asymptotic polymerization reaction creates the speed problem, especially at low levels of water. Thus, under cell conditions the reaction more accurately is:

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O \rightarrow \quad \text{(v)}$$

$$H_4P_2O_7 \rightarrow H_5P_2O_{10} \rightarrow H P_4O_{13} \rightarrow \quad \text{(vi)}$$

in a polymerization reaction to

$$2HPO_3 + \text{the other water molecule} \quad \text{(vii)}$$

As the reaction occurs, the rate of reaction slows due to the glass-like form of the product of the reaction and the resultant limited availability and mobility of the H and OH to the electrodes. Thus, it is apparent that the rate of reaction can be substantially increased if it is possible to stop the polymerization reaction and prevent the molecule from getting too big. Advantageously the reaction should be controlled so that it proceeds from the monomer to the dimer and then back again.

The instant invention prevents the polymerization reaction from occurring by utilizing an acid having blocked polymerization sites. The polymerization reaction is prevented and at the same time hygroscopicity of the material is maintained. For example, if the phosphoric acid has organic groups substituted for the hydroxy groups the polymerization sites are blocked.

$$2R{-}\overset{\overset{O}{\|}}{\underset{\underset{R'}{|}}{P}}{-}OH \rightleftarrows H_2O + R{-}\overset{\overset{O}{\|}}{\underset{\underset{R'}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{R'}{|}}{P}}{-}R \quad \text{(viii)}$$

In the structure shown, R and R′ are organic groups and may be the same or different. As can be seen the acid is changed to an anhydride when current is used in the cell. The water absorption is the reverse reaction, anhydride to acid. This indicates that any anhydride having blocked

polymerization sites is potentially useful in the cell. However, the efficiency of the cell involves mols of material per mol of water. Thus the molecular weight of the material being used for the electrolyte affects the ratio and a higher molecular weight electrolyte decreases the chemical efficiency of the cell. Also, the molecules become more unwieldy with increasing molecular weight. Therefore, the invention is desirably limited to the use of acids containing not more than the equivalent of 19 carbon atoms with the core atom, in this case phosphorous, being counted as an equivalent carbon atom. When heavier elements are used for the core atom, then the total number of equivalent carbon atoms (i.e. the actual carbon atoms and the core atom) will desirably be lower than 19, as is obvious to those skilled in the art.

Depending upon the cell materials and the particular electrolyte to be used in the cell, the material may be applied in either the acid or anhydride form. For convenience, the anhydride shall be referred to as the electrolyte.

As an example of the instant invention, dimethyl phosphinic acid was prepared according to the following reactions:

$$4CH_3MgCl + 2PSCl_3 \longrightarrow 2(CH_3)_2PS(MgCl)_2 \quad (ix)$$

$$2(CH_3)_2PS(MgCl)_2 + 4HOH \xrightarrow{H_2SO_4} [(CH_3)_2PS]_2 + 4Mg(OH)C \quad (x)$$

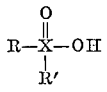
$$[(CH_3)_2PS]_2 + H_2O_2 \longrightarrow 2(CH_3)_2PO(OH) + 2H_2S \quad (xi)$$

Using a 2 liter round bottom flask fitted with a mechanical stirrer, a reflux condenser with drying tube, and a pressure equalizing addition funnel, and which was immersed in a cold bath at −12° C. (10° F.), 104 grams of thiophosphoryl chloride was added dropwise with stirring in two hours to 2 mols of methyl magnesium chloride and 750 milliliters of anhydrous ether. The reaction mixture was maintained at −8 to −3° C. (17–26° F.) internal temperature during the addition. After the addition the cooling bath was slowly lowered away from the flask over a two hour period with continuous stirring. The reaction mixture was allowed to warm up to room temperature and slowly poured into a mixture of 200 milliliters of concentrated sulphuric acid and 2 kilograms of crushed ice. After the addition was complete the mixture was allowed to stand one hour with occasional stirring. The mixture was filtered and the white solid washed with water and a small amount of ether and vacuum dried over night. The solid was recrystallized from a hot mixture of 1—1 ethanol-benzene and air dried. The intermediate $[(CH_3)_2PS]$ had a melting point of 229.5–230.5° C. (445–447° F.) and was added to 60 milliliters of carbon tetrachloride in a 300 milliliter flask and brought to reflux. Twenty-five milliliters of 30% hydrogen peroxide was then added slowly with stirring. The mixture was refluxed an additional two hours with stirring, cooled, and filtered with the filtrate separating into two phases. The aqueous phase was dried in vacuum over phosphorous pentoxide and the product recrystallized twice from hot benzene. The yield was 3.9 grams of material melting at 88.5 to 91.5° C. (191–197° F. This material, in the form of a 20% by weight solution, was then used to coat three cells of the Keidel type utilizing the technique described in U.S. Pat. 3,240,693 to Douglas B. Gardner.

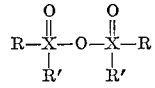
The cell was abruptly exposed to about a 25% relative humidity vapor. As shown in FIG. 1, a conventional electrolytic cell was slow to sense (zone X) and responded relatively slowly (zone Y) to the sudden change in humidity. A typical response time would be about two and a half minutes.

Referring now to FIG. 2 it may be seen that the cell containing the electrolyte according to the instant invention was quick to sense (zone X') and responded quite rapidly (zone Y') to the large step change in humidity. In fact, the response time was less than thirty seconds.

Although in the above example R and R' were both methyl groups, it will be appreciated the invention is not limited thereto. Any suitable organic group can be used to block the polymerization sites, such as alkyl groups, aryl groups, or substituted alkyl, or substituted aryl groups. R and R' may be either the same or different. Similarly the material is not limited to dimethyl phosphinic acid. Practically any anhydride having blocked polymerization sites and containing not more than the equivalent of about 19 carbon atoms can be used effectively in the practice of the instant invention. Thus, the anhydride can be formed from an acid of an element selected from the group consisting of aluminum, boron, Group IV–A elements, and Group V–A elements, so long as the polymerization sites are blocked and the molecule contains not more than the equivalent of 19 carbon atoms. When the Group V–A compounds are used, the blocked acid has the following structural formula:



and the anhydride:



in which R and R' are organic groups, H is hydrogen, O is oxygen, and X is selected from the group consisting of nitrogen, phosphorous, arsenic, antimony, and bismuth.

When the material is a blocked acid of a Group IV–A element, the blocked acid has the following structural formula:



and the anhydride:

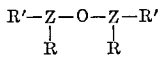


in which R is an organic group, O is oxygen, H is hydrogen, and Y is selected from the group consisting of carbon, silicon, germanium, tin, and lead.

When aluminum or boron are used as the core element, the structure in its blocked form is more accurately that of a hydroxide than of an acid but may still be referred to as blocked acid. Thus, the blocked acid of these two elements would have the following structural formula:



and the anhydride:



in which R and R' are organic groups, H is hydrogen, O is oxygen, and Z is selected from the group consisting of boron and aluminum.

Typical anhydrides useful as electrolyte materials according to the instant invention are acetic anhydride, acetic propionic anhydride, n-valeric anhydride, isovaleric anhydride, dichloroacetic anhydride, caproic anhydride, n-heptoic anhydride, benzoic anhydride, lauric anhydride, chloroacetic anhydride, itaconoic anhydride, stearic anhydride, m-toluic anhydride, phenylacetic anhydride, o-chlorobenzoic anhydride, m-chlorobenzoic anhydride, p-toluic anhydride, 4-nitrophthalic anhydride, cinnamic anhydride, phthalic anhydride, o-nitrobenzoic anhydride, α-naphthoic anhydride, m-nitrobenzoic anhydride, 3-nitrophthalic anhydride, 1,2-naphthalic anhydride, p-nitrobenzoic anhydride, p-chlorobenzoic anhydride, d-camphoric anhydride, 2,3-naphthalic anhydride, 1,8-naphthalic

anhydride, tetrabromophthalic anhydride, and tetraiodophthalic anhydride. Other useful anhydrides include dimethyl phosphinic anhydride, methyl propyl phosphinic anhydride, ethyl hexyl phosphinic anhydride, dioctyl phosphinic anhydride, and octyl decyl phosphinic anhydride. All the elements mentioned above make blocked acids and blocked anhydrides similar to those of carbon and phosphorous. If a blocked acid of nitrogen is being used, it is desirable to keep the organic groups large enough so that the material is either a liquid or solid rather than a gas.

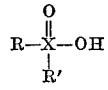
While there have been shown and described hereinabove certain embodiments of this invention, it is to be understood that the invention is not limited thereto and that various changes, alterations, and modifications can be made thereto without departing from the spirit and scope thereof as defined in the claims.

What is claimed is:

1. In a hygrometer electrolytic cell adapted for the determination of water content of a gas or liquid sample wherein the cell comprises an electrolyte material which is hygroscopic to water and wherein means are provided for electrolyzing the water absorbed by the electrolyte to provide an indication of the amount of water in the gas or liquid sample, the improvement wherein the electrolyte material is an anhydride formed from an acid of an element selected from the group consisting of aluminum, boron, Group IV–A elements, and Group V–A elements, and having blocked polymerization sites, and containing not more than the equivalent of 19 carbon atoms.

2. The electrolytic cell of claim **1** wherein the polymerization sites in the acid are blocked by organic groups.

3. The electrolytic cell of claim **2** wherein the blocked acid has the following structural formula:



in which
R and R′ are organic groups;
H is hydrogen;
O is oxygen; and
X is selected from the group consisting of nitrogen, phosphorous, arsenic, antimony and bismuth.

4. The electrolytic cell of claim **3** wherein the blocked acid is dimethylphosphinic acid.

5. The electrolytic cell of claim **3** wherein R and R′ are selected from the group consisting of alkyl groups, aryl groups, substituted alkyl groups, and substituted aryl groups.

6. The electrolytic cell of claim **3** wherein R and R′ are identical organic groups.

7. The electrolytic cell of claim **3** wherein R and R′ are different organic groups.

8. The electrolytic cell of claim **2** wherein the blocked acid has the following structural formula:



in which
R is an organic group;
O is oxygen;
H is hydrogen; and
Y is selected from the group consisting of carbon, silicon, germanium, tin, and lead.

9. The electrolytic cell of claim **8** wherein R is selected from the group consisting of alkyl groups, aryl groups, substituted alkyl groups, and substituted aryl groups.

10. The electrolytic cell of claim **2** wherein the blocked acid has the following structural formula:



in which
R and R′ are organic groups;
H is hydrogen;
O is oxygen; and
Z is selected from the group consisting of boron and aluminum.

11. The electrolytic cell of claim **10** wherein R and R′ are selected from the group consisting of alkyl groups, aryl groups, substituted alkyl groups, and substituted aryl groups.

12. The electrolytic cell of claim **10** wherein R and R′ are identical organic groups.

13. The electrolytic cell of claim **10** wherein R and R′ are different organic groups.

14. The electrolytic cell of claim **2** wherein the anhydride is selected from the group consisting of acetic propionic anhydride, propionic anhydride, isobutyric anhydride, n-butyric anhydride, n-valeric anhydride, isovaleric anhydride, dichloroacetic anhydride, caproic anhydride, n-heptoic anhydride, benzoic anhydride, lauric anhydride, chloroacetic anhydride, itaconic anhydride, stearic anhydride, m-toluic anhydride, phenylacetic anhydride, o-chlorobenzoic anyhdride, m-chlorobenzoic anhydride, p-toluic anhydride, 4-nitrophthalic anhydride, cinnamic anhydride, phthalic anhydride, o-nitrobenzoic anhydride, α-naphthoic anhydride, m-nitrobenzoic anhydride, 3-nitrophthalic anhydride, 1,2-naphthalic anhydride, p-nitrobenzoic anhydride, p-chlorobenzoic anhydride, d-camphoric anhydride, 2,3-naphthalic anhydride, 1,8-naphthalic anhydride, tetrabromophthalic anhydride, and tetraiodophthalic anhydride.

15. The electrolytic cell of claim **2** wherein the anhydride is selected from the group consisting of dimethyl phosphinic anhydride, methyl propyl phosphinic anhydride, ethyl hexyl phosphinic anhydride, dioctyl phosphinic anhydride, and octyl decyl phosphinic anhydride.

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GERALD L. KAPLAN, Primary Examiner

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73—336.5; 204—1 T; 260—502.4 R; 324—29