March 28, 1944. G. A. PERLEY 2,345,498

SALT-BRIDGE TUBES AND METHODS OF PRODUCING THEM

Filed April 1, 1942

Fig. 1

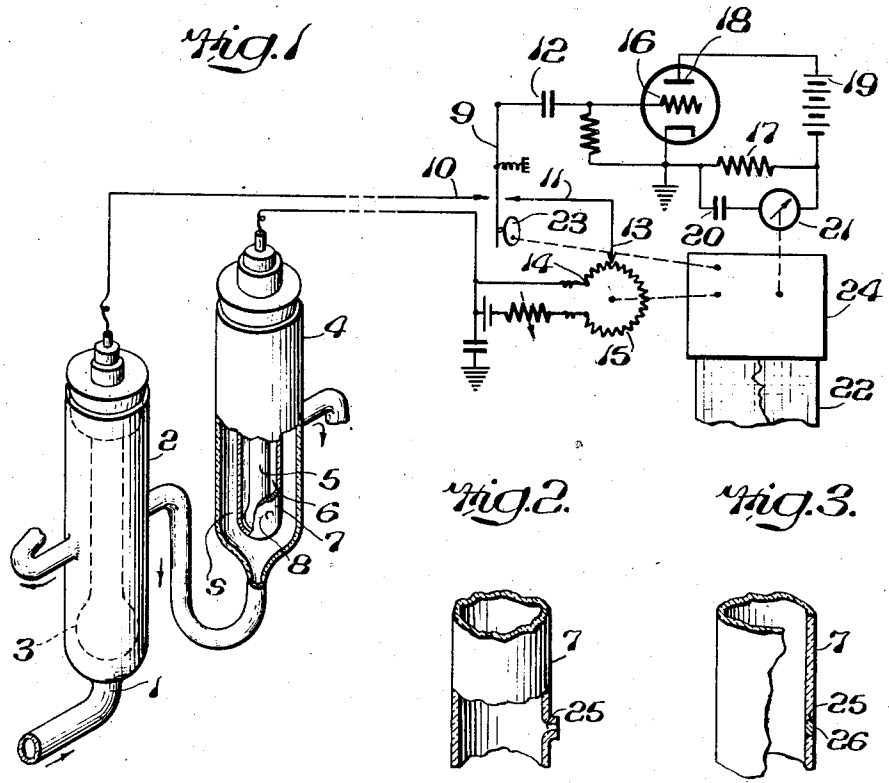


Fig. 2

Fig. 3

Fig. 4

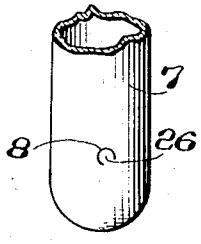


Fig. 5

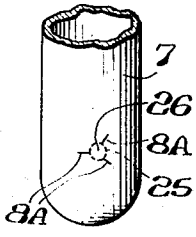


Fig. 6

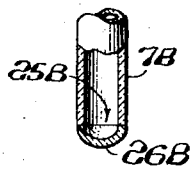
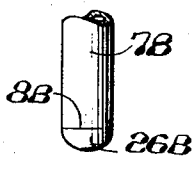


Fig. 7



INVENTOR.
GEORGE A. PERLEY

C. S. Ethret

ATTORNEY.

Patented Mar. 28, 1944 2,345,498

UNITED STATES PATENT OFFICE

2,345,498

SALT-BRIDGE TUBE AND METHOD OF PRODUCING IT

George A. Perley, Wyncote, Pa., assignor to Leeds and Northrup Company, Philadelphia, Pa., a corporation of Pennsylvania

Application April 1, 1942, Serial No. 437,153

7 Claims. (Cl. 204—195)

My invention relates to salt-bridge tubes such as employed with reference electrodes of ion-concentration cells, and more particularly relates to methods of making, in a salt-bridge tube, a minute passage comprised in or constituting the salt-bridge connection providing for diffusion of the salt-bridge solution into another solution exterior to the salt-bridge tube and for electrical conduction between the two solutions.

In accordance with my invention, while the glass constituting the salt-bridge tube is at temperature sufficiently high to render it tacky, a small hole therein is sealed by a plug of material, such as another glass, having different, preferably higher, coefficient of expansion so that, upon cooling of the glasses, there is produced a crack or slit having the hereinafter described advantages for forming a salt-bridge connection.

My invention further resides in the salt-bridge tubes and methods of making them hereinafter described and claimed.

For an understanding of my invention, reference is made to the accompanying drawing, in which:

Fig. 1, partly diagrammatic, illustrates a typical arrangement for recording changes in ion-concentration;

Figs. 2 to 4 illustrate successive stages of formation of a salt-bridge tube shown in Fig. 1;

Fig. 5 illustrates a modification of the salt-bridge tube of Fig. 4.

Figs. 6 and 7 illustrate another modification of my invention.

Referring to Fig. 1 as exemplary of a system with which the invention may be employed, solution S whose hydrogen-ion concentration or hydroxyl-ion concentration, generically termed pH, is to be measured, is passed through the flow channel 1, which may be generally of the type disclosed in my United States Letters Patent 2,108,293, comprising a chamber 2 in which is disposed a suitable measuring electrode, for example a glass electrode 3, and a chamber 4 in which is disposed a suitable reference electrode 5. Between the reference electrode and solution S is interposed a salt-bridge comprising a suitable salt-bridge solution 6, for example potassium chloride, confined within tube 7 having an opening or salt-bridge connection 8, of character hereinafter more fully explained, affording a path for electrical conduction between the reference electrode 5 and the solution S.

The difference of potential developed by the ion-concentration cell comprising the measuring and reference electrodes, may be measured by any suitable system, such for example as disclosed in United States Letters Patent 2,108,294, or 2,285,482, or application Serial No. 457,845, Williams filed September 10, 1942.

In the system shown in Fig. 1, which is claimed in aforesaid Williams application, the movable contact member 9 is moved alternately to engage first one and then the other of the contacts 10, 11; each time the contact 9 is moved into engagement with contact 10, the condenser 12 is subjected to voltage developed by the ion-concentration cell 3, 5 and each time contact 9 engages the fixed contact 11, the condenser 12 is subjected to the effective voltage of potentiometer 15, i. e., the potential difference existing between slide-wire contact 13 and a terminal 14 of the slide-wire. If these two voltages are equal, the connection of condenser 12 alternately to the ion-concentration cell and to the potentiometer slide-wire effects no flow of displacement current to or from condenser 12; in consequence, the potential of the grid 16 of tube V remains constant and there is no change in magnitude of current traversing resistance 17 in circuit with the anode 18 of the tube V and a suitable source of current, such as battery 19.

When, however, the fixed contacts 10 and 11 are not at the same potential, due for example to change in the pH of solution S, the movement of contact 9 from engagement with one to the other of the fixed contacts causes flow of displacement current to or from condenser 12 and accordingly the potential of the grid 16 is decreased or increased and therefore causes, because of its effect upon the anode current of tube V, change in magnitude of the voltage drop across the resistance 17.

Upon increase or decrese of the voltage drop across resistance 17, displacement current flows to or from the condenser 20 connected in series with galvanometer 21 across resistance 17. As more fully explained in the aforesaid Patent 2,285,482 to Wunsch, the deflections of the galvanometer are utilized to effect a rebalancing adjustment of the movable element of the potentiometer slide-wire 15 and to position a pen or equivalent marker element which traces upon the chart or sheet 22 a curve representing the variation, with time, of the selected ion-concentration of solution S. The oscillation of contact 9 between contacts 10 and 11 may be effected by cam 23 driven at constant speed by connection for example to a suitable shaft of the mechanism 24, preferably of the type disclosed in United States Letters Patent 1,935,732, Squibb.

In ion-concentration measuring systems in general, the path providing for electrical conduction between the salt-bridge solution and the test solution have been either of the type comprising ground glass plugs, closed stop-cocks, ground joints, asbestos fibres, wicks, clamped rubber tubes, agar gel and the like, or of the type including cylindrical openings of small diameter, small capillary tubes, and the like.

A serious disadvantage of the first group precluding their satisfactory use in industrial recording systems is that they require the bridge opening, region of contact between the bridge and test solutions, frequently to be cleaned or renewed as otherwise there are established secondary junction potentials of magnitude corresponding with intolerable error. In many of the salt-bridge connections of the first type or group, there are a multitude of paths for diffusion of the salt-bridge solution into the test solution as well as for the reverse diffusion of the test solution in the salt-bridge solution; the mechanical resistance to flow of the salt-bridge solution may vary greatly in the different paths yet all paths may contribute in the interchange of ions between the salt-bridge and test solutions with the result there is often, and usually, ultimately established a "constrained diffusion" type of junction which is a source of serious variation in potential and therefore of error of measurement. When this type of junction is used it is desirable or necessary that the junction be flushed before each pH measurement and that fresh salt-bridge solution be supplied at the interface, contact plane of the salt-bridge and test solutions, each time a liquid junction is formed. In industrial recording of pH, it is not feasible to make the frequent cleansing or renewal operations necessary to insure reasonably high accuracy of the pH measurments.

A serious disadvantage of the second type or group of salt-bridge connections, those comprising cylindrical openings of small diameter, is the need for relatively large volumetric flow of the salt-bridge solution to avoid contamination of the salt-bridge solution by back diffusion thereinto of the test solution. Consequently the maintenance and cost of operation of such type junction is excessive particularly when, as in industrial applications, continuous measurements of pH are desired.

Another disadvantage of this type of salt-bridge connection is that it may to varying extent be blocked by particles of solid matter, for example precipitate from the salt-bridge solution.

In accordance with the present invention, the salt-bridge connection or opening is provided by a crack or slit 8 of such extremely narrow width, for example from about .000025 centimeter to preferably not more than about .0005 centimeter, that the velocity through and from the salt-bridge connection is so high there is no possibility of contamination of the salt-bridge solution by back diffusion of the test solution; more particularly, the velocity is within the range of from about 10 cm. per hour to about 60 cm. per hour although the volumetric rate of flow is so low, for example .002 cubic centimeter per hour to .02 cubic centimeter per hour that the maintenance cost of salt-bridge solution for continuous recording is negligible. It is feasible to record the pH of solutions during processing in which the liquid junction of the salt-bridge is subjected to pressure differences as high as 28" of mercury; even when the salt-bridge solution is subjected to such high differential pressure continuous recording of pH for long periods of time, weeks, is entirely, and for the first time, practical.

Though not limited thereto, there are described herein several preferred methods of making junctions of the crack or slit type which in practice have proved most satisfactory. One of these methods, Figs. 2–4, involves heating the tube 7, preferably before the lower end is formed, to temperature sufficiently high to render it soft and tacky; a pointed hook-shaped tool is then inserted through the open end of the tube and forced against the side to make a small passage or opening 25, Fig. 2. The cross sectional area of this opening may correspond, for example, with the area of a circle of about 1.5 millimeters diameter, though the hole is not necessarily circular in cross section; the thickness of the tube wall may be about 1 millimeter. While the glass of tube 7 is still soft and tacky a small molten or tacky globule of another glass, one having suitably different temperature coefficient of expansion, is brought into engagement with opening 25 and is drawn into it by capillary action. This globule forms a block or plug 26, Fig. 3, completely filling or sealing the opening 25 and more or less fused into or bonded to the glass comprising the tube 7; when the difference in the temperature coefficients is small, the seal is preferably what is termed in the glass-blowing art as a "cold" seal.

When the seal plug 26 is of glass having higher temperature coefficient of expansion than the glass comprising tube 7, it shinks during cooling more rapidly than the tube wall and as a result there is produced, Fig. 4, a crack, fracture or slit 8 extending to greater or less extent about the plug. The length and width of the crack may be reasonably closely determined by selection of glasses having suitably different temperature coefficients of expansion and by selection of the cross-sectional area of opening 25; in general, the smaller the difference between the coefficients of expansion of the glasses comprising tube 7 and plug 26, the narrower is the slit or crack 8. As in the other modifications, the slit is too narrow to be blocked by particles of solid matter which may be present or formed in the salt-bridge solution.

By way of example, the following table indicates characteristics of the salt-bridge connections made in accordance with the foregoing method from various glasses therein identified.

	Manufacturer designation	Coefficient °C. of linear expansion	Average width of crack in cm.	Electrical resistance in ohms	
				Saturated KCl	.1 normal KCl
Tube	Corning Pyrex (No. 774)	32×10^{-7}			
Plug	Corning Lead (No. 001)	90×10^{-7}	480×10^{-6}	1,170	35,000
Do	Corning Code (No. 881)	88×10^{-7}	340×10^{-6}	2,650	55,000
Do	Kimball N51a	49×10^{-7}	50×10^{-6}	12,000	363,000

(The electrical resistance of the salt-bridge connection is measured with salt-bridge solution inside and outside of the tube; when lower resistance is desired one or more additional salt-bridge connections may be made in the same tube in accordance with the methods herein described.)

The surfaces of the passage defined by the crack have the extreme smoothness or gloss of a glass fracture and so offer inappreciable frictional resistance to flow of the salt-bridge solution. Aside from other considerations, potassium chloride is preferred over other salt-bridge solutions in the crack type of salt-bridge connection because of its lower viscosity (10.95 millipoises at 20° C.).

It is usually not detrimental to satisfactory performance if the crack 8 extends entirely about the plug because its almost inevitable dissymmetry locks the plug firmly in position.

When the glass comprising tube 7 is of the higher coefficeint of expansion, upon cooling of the tube and plug, Fig. 5, one or more short cracks 8A extending away from the boundary of the plug and tube through the tube wall are formed. These cracks afford a salt-bridge connection having substantially the same desirable characteristics including constancy of junction potential, within about .003 volt over long periods of uninterrupted use, as the modification shown in Fig. 4.

Particularly when the salt-bridge tube, or at least the end of it immersed in the test solution must be of relatively small diameter, for example about 3.5 millimeters, the method and construction illustrated in Figs. 6 and 7 is preferred.

The opening 25B at one end of tube 7B is sealed by a globule of glass having a suitably different temperature coefficient of expansion. After the globule has fused or bonded to the end of the tube and while both are still at high temperature, the open end of tube 7B is blown into to shape the globule into a plug or thimble 26B. As the assembly cools, a crack 8B is produced due to the different rates of contraction of the two glasses; the crack extends through the wall and to greater or less extent around the periphery of the tube at the junction of the two glasses. The salt-bridge connection afforded by crack 8B has the same desirable operating characteristics discussed above in connection with the other modifications.

In selection of the glasses for all modifications, the glass comprising the tube or body, 7 or 7B, should be of relatively high chemical and mechanical resistance; the glass comprising plug 26 or 26B should, for long life, be of relatively high chemical resistance but, without appreciable effect upon accuracy of the measurement, may be of less chemically resistant glass. The range of choice of suitable glasses is of course wider when the salt-bridge tube is to be used only in a predetermined portion of the pH range rather than throughout a range from 0 pH to 14 pH.

What I claim is:

1. The method of forming a passage for a salt bridge connection through the wall of a salt bridge tube which comprises forming a small hole through said wall, heating the tube to temperature effecting tackiness of the glass comprising it, closing the hole in the heated tube with a plug of another glass having substantially different coefficient of expansion, and thereafter cooling the tube to produce, because of different rates of contraction of the glasses, a crack at or adjacent the plug.

2. The method of forming a passage for a salt bridge connection through the wall of a salt bridge tube which comprises forming a small hole through said wall, heating the tube to temperature effecting tackiness of the glass comprising it, closing the hole in the heated tube with a plug of another glass having higher coefficient of expansion, and thereafter cooling the tube and plug to produce, because of different rates of contraction of the glasses, a crack around the plug.

3. The method of forming a passage for a salt bridge connection through the wall of a salt bridge tube which comprises forming a small hole through said wall, heating the tube to temperature effecting tacky state of the glass comprising it, closing the hole in the heated tube with a plug of another glass having lower coefficient of expansion, and thereafter cooling the tube and plug to form, because of different rates of contraction of the glasses, a crack in the tube extending away from the plug.

4. The method of forming a passage for a salt-bridge connection through a salt-bridge tube of glass which comprises heating the tube to temperature effecting tackiness of the glass around an opening in the tube, closing the opening with a plug of glass having substantially different coefficient of expansion, and thereafter cooling the tube to produce, because of different rates of contraction of the glasses, a crack at or adjacent the plug.

5. The method of forming a passage for a salt-bridge connection through a salt-bridge tube of glass which comprises heating an open end of the tube to temperature effecting tackiness of the glass, closing the open end of the tube with a plug of glass having substantially different coefficient of expansion, and thereafter cooling the tube to produce, because of different rates of contraction of the glasses, a crack extending peripherally of the tube at the junction of the glasses.

6. A salt-bridge tube having a wall of glass, a plug of glass fused to said wall and having a coefficient of expansion different from that of the glass of said wall, and for a salt-bridge connection in said wall, at least one crack in contact with said plug and of width not exceeding about .0005 centimeter.

7. A salt-bridge tube having a wall of glass, a plug of glass fused to said wall and having a coefficient of expansion higher than that of the glass of said wall, and for a salt-bridge connection in said wall, at least one crack around said plug and of width not exceeding about .0005 centimeter.

GEORGE A. PERLEY.