No. 658,891. Patented Oct. 2, 1900.

H. CARMICHAEL.

ELECTRODE AND ELECTRODE CONNECTION.

(Application filed May 11, 1899.)

(No Model.)

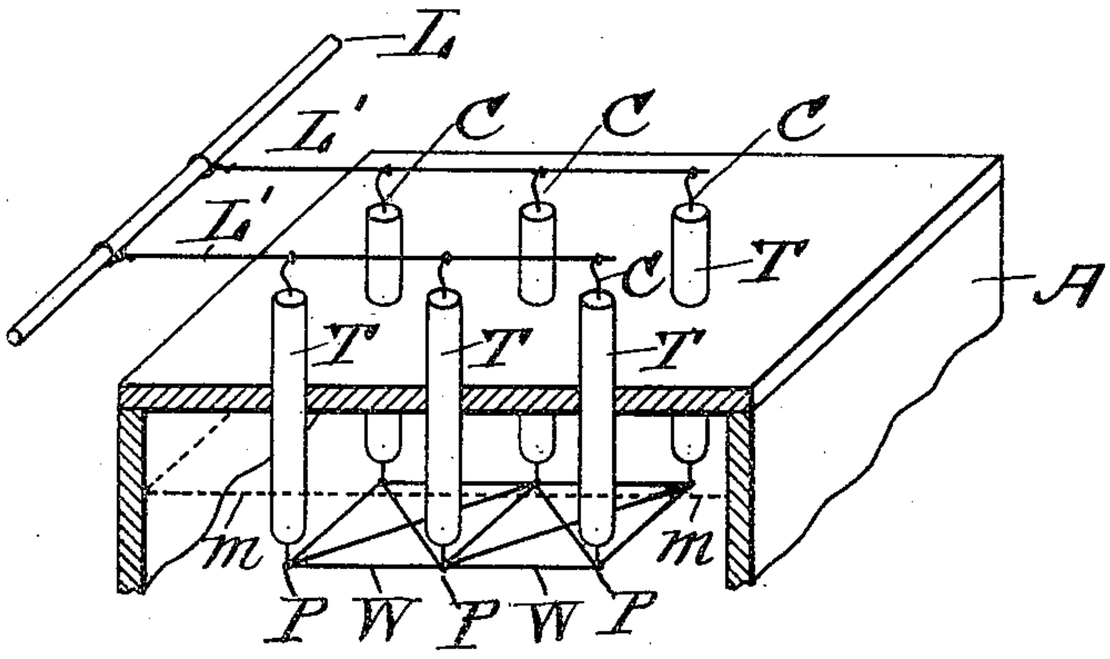

Fig. 1.

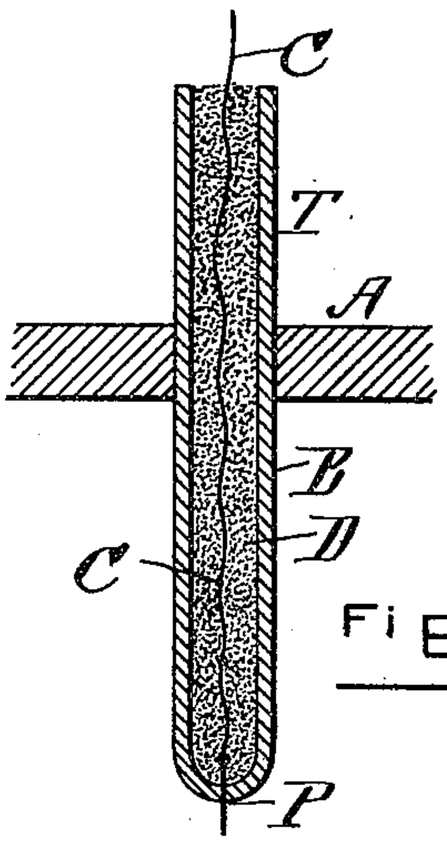

Fig. 2.

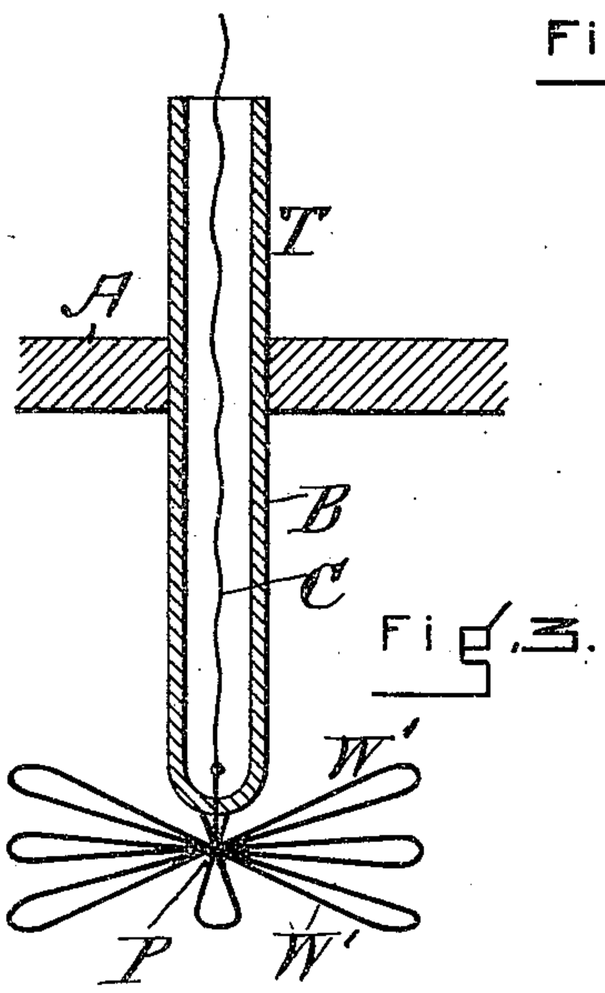

Fig. 3.

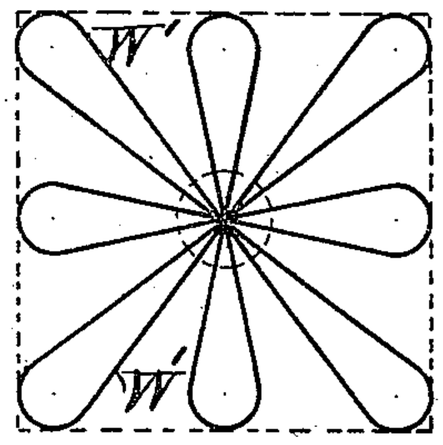

Fig. 4.

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ELECTRODE AND ELECTRODE CONNECTION.

SPECIFICATION forming part of Letters Patent No. 658,891, dated October 2, 1900.

Application filed May 11, 1899. Serial No. 716,373. (No model.)

To all whom it may concern:

Be it known that I, HENRY CARMICHAEL, a citizen of the United States of America, and a resident of Malden, county of Middlesex, and State of Massachusetts, have invented certain new and useful Improvements in Electrodes and Electrode Connections, of which the following is a specification.

The object of the invention and improvements herein described is the provision of improved electrodes and their connections for electrolytic and analogous apparatus wherein precautions against corrosion of the conductors and their contact-joints are rendered necessary by the character of the substances which are subjected to the process carried on in the apparatus or which form products of the process. A typical example of such apparatus and processes will be found described in my United States patent for a method of and apparatus for electrochemical decomposition, No. 518,710, issued April 24, 1894. The process therein described for obtaining the products of electrolysis of a solution of sodium chlorid is characteristic, in that the caustic alkali and chlorin which are developed in the course of the process are substances which in the presence of the electric current become exceptionally troublesome by reason of their corrosive activity and the persistence with which they insinuate themselves into and through the most carefully prepared and protected joints in an apparatus and their capacity for destroying in the most unexpected manner materials which, under ordinary conditions, are confidently regarded as inert and refractory. My present invention and improvements will therefore be described and illustrated in connection with a sodium-chlorid electrolysis and apparatus therefor, although doubtless they will be found useful and adaptable in other situations. The cathode construction of the apparatus shown in my patent aforesaid has been found to offer no difficulties in construction or operation; but the predicament of the anode, which is subjected to the action of free chlorin in the presence of an electric current, is very different. The anode of the apparatus thus described has proved fairly effective and economical and has demonstrated by prolonged commercial working on a large scale that its fundamental scheme of arrangement and construction is correct. Broadly speaking, the anode of the patent aforesaid is an electrode which consists of two systems—first, an internal system of corrodible conductors surrounded and insulated by non-corrodible material, and, second, an external system of uninsulated non-corrodible conductors, the internal and external systems being connected electrically by non-corrodible metallic pins, which pass through the insulation of the internal system in such manner as to exclude all corrosive agents from the internal system, while maintaining and preserving good electrical contact with the external system. By this arrangement such non-corrodible metallic conductors as platinum are used with a minimum of expense, the cheaper corrodible conductors being used to the point where exposure of the conductor is essential to the carrying on of the process.

The improvements which form the subject-matter of the present description involve the invention of the general scheme outlined in the patent aforesaid, and consist of improvements in the structural arrangement by which the general two-system scheme shall be rendered more effective and its adoption more convenient and in the special construction of the internal system of corrodible conductors enveloped in non-corrodible non-conductors. The specific mode of carrying this general scheme into effect, which is described in my patent aforesaid, consisted in the use of a copper wire incased in a lead tube, which was in turn incased in a rubber sleeve. Through the lead and rubber were driven short platinum pins, which served as pegs on which to stretch the network of fine platinum wires which completed the metallic portion of the exposed electrode. The covering and insulating materials which incased the copper wire—viz., rubber and lead—were such as had proved adequate in other structural combinations to resist the action of chlorin and salt solutions in apparatus previously used and were adopted confidently for my apparatus and process; but the process described in my patent aforesaid differs radically from prior processes in that it is continuous instead of intermittent, and therefore involves a higher concentration of the products of

electrolysis than had theretofore been practicable in non-continuous and non-progressive electrolysis. There was, therefore, a far more severe demand made upon the apparatus and its component parts than in prior apparatus, and the frequent opportunities for examination and renewal of worn-out portions which the interruptions of intermittent processes had afforded in older apparatus were withdrawn when the apparatus of my patent aforesaid went into commercial use. The process of that patent is and proved to be permanently continuous and called for an apparatus which should be as nearly as possible indestructible. The continuity of the process soon developed the fact that improvements in the anode were necessary in order to render that part of the apparatus as durable as the other parts. The new condition exacted requirements in structural features which had not, so far as I am aware, developed in the use of apparatus for intermittent and non-progressive electrolysis. While the specific form of anode described in the patent aforesaid performed its office perfectly well for a time—a much longer time than the periods of activity in intermittently-operated apparatus—that form of anode proved in practice to be structurally the relatively weak point in the system when compared with the rest of the apparatus, which has proved to be practically more permanent. The constant action of chlorin in solution developed unusual and unexpected irritant capacity in the presence of the electric current, which seems to give the chlorin and the chlorinated solution the power to insinuate themselves into the very body of the insulator. This phenomenon also developed itself in experimenting with other insulators than rubber, even glass showing a tendency after a while to crackle into minute granules, the interstices between the granules gradually permitting the solution to penetrate to the corrodible conductor which was inclosed by the glass. Glass tubes may, however, be considered fairly effective in the structural arrangement hereinbelow described, although when the apparatus is used for the continuous electrolysis of sodium chlorid another substance is to be preferred and enters into the subject-matter of the invention hereinbelow described. The above and similar experiments showed conclusively that substances which under ordinary conditions are good permanent insulation under the conditions which prevail in an electrolytic apparatus are short-lived and ineffective.

My invention hereinbelow described consists of, first, an electrode constructed on the internal and external system, having for its protective portion a material discovered to be practically permanent as an insulator under electrolytic conditions, and, second, an arrangement of an electrode of the two-system type which, aside from the special materials of which it is composed, possesses increased advantages and novel characteristics, due to constructive features rather than to the selection of special materials.

In the drawings, Figure 1 is a vertical cross-section and perspective view of the upper part of an electrolytic cell, showing the anode construction. Fig. 2 is a detail showing one of the leading-in drop-tubes of Fig. 1 in cross-section. Fig. 3 is a detail showing an arrangement of individual electrodes, and Fig. 4 is a plan view of an electrode attached to the device shown in Fig. 3.

In Fig. 1 the upper portion of an anode-compartment is shown in perspective and vertical cross-section. A full representation of an electrolytic apparatus containing an anode-chamber like the one partially shown in Fig. 1 may be seen in Fig. 2 of my patent aforesaid. The walls and cover of the anode-chamber A are composed of slate or other proper material, and the cover thereof is pierced at suitable intervals for the passage of pocket-shaped ducts T, which penetrate into the anode-chamber, so that their lower extremities pass below the level of the electrolyte in the anode-chamber, which is indicated in Fig. 1 by the dotted line *m*.

Fig. 2 shows in cross-section on an enlarged scale one of the pocket-shaped ducts T. The specific form of pocket-duct used herein for illustration is a tube B, closed at its lower end and open at its upper end. In general shape it is like the ordinary test-tube of the laboratory. This is a form which I consider advantageous, because of its simplicity and the ease with which each pocket-shaped duct of this form can be manipulated in making electric connections inside and outside and in attaching to the cover of the apparatus. At the closed end of the tube T, which I term a "drop-tube," a short pin P, of non-corrodible conducting material, such as platinum, is fused into the wall of the drop-tube or otherwise hermetically sealed therein, preferably by the material of which the tube is composed, leaving the ends of the pin emerging from the wall of the drop-tube, one end protruding therefrom into the electrode-compartment of the apparatus, the other end intruding within the drop-tube itself. The protruding end of the pin I is adapted to the attachment of the exposed portions of the electrode. A conducting-wire C, composed of copper or some other corrodible conductor which is inexpensive as compared with the non-corrodible conductor, is electrically attached to the intruding end of the pin P and leads therefrom out of the external end of the tube T and, as shown in Fig. 1, is attached to the feed-wire L or a branch L′ therefrom. In order still further to secure the permanent insulation of the conductor C, the tube T may be filled or packed with a viscous insulating material D, such as asphalt, resinous substances, or such paraffinoid products as ceresite or mixtures of such substances. The melting-point of ceresite I may raise by admixture of carnauba-

wax. The operation of an electrolytic apparatus usually involves a considerable rise in temperature, which increases the fluidity of the viscous insulator which has been run into the tube T, so that if there should happen to be formed any break or interstice in the wall of the drop-tube T the viscous material D will by its increased fluidity offset any tendency of the electrolyte to penetrate to the conductor C. This precaution, while entirely commendable, is, however, probably unnecessary, provided a reliable material is used in the construction of the drop-tube T or equivalent pocket-shaped duct, so that the arrangement shown in Fig. 3, where no viscous insulation is employed, may be adopted without fear of diminishing the protection which must surround the conductor C.

The arrangement of the actively-operative electrode may be such as shown in Fig. 1, where platinum wires W are strung from the pins P and form a network horizontally disposed in the electrode-chamber A, in which case the electrode is electrically a unit. An arrangement which is, however, I believe, to be preferred is that shown in Figs. 3 and 4, where each drop-tube carries a separate and independent electrode composed of wires which radiate from the pin P as a central support. The form which I prefer for these individual electrodes consists of a group or rosette composed of several radiating loops W′, of platinum wire, which can be fused to the pin P. The shape of the area covered by the radiating loops should be determined by the disposition of the drop-tubes T, the object being to cover thoroughly the entire area in the electrode-chamber, so if the drop-tubes T are arranged as in Fig. 1 each one of the loop rosettes should occupy an area substantially square, and all the rosettes will in the aggregate cover the available surface. For this purpose the arrangement shown in Fig. 4 is preferred, where the diagonals of the square are covered by long loops and the diameters of the square by the shorter loops.

The advantages of the form of electrode and electrode connections above described can be secured by the use of any insulating material in the construction of the pocket-shaped ducts, and these advantages will persist as long as the material lasts. The material which I have adopted for use in connection with electrolysis of common salt solution after observing the unexpected failure of sundry substances, which had been confidently relied on to perform their function satisfactorily and permanently, is vitrified non-absorbent porcelain. "Vitrified porcelain" is porcelain which is "fritted" together in all its parts as distinguished from being merely glazed on the surface. Glazed porcelain is non-absorbent to the extent of its superficial protection, but the interior remains absorbent-like biscuit-ware. A non-absorbent vitrified porcelain has the glaze effect all the way through its mass and is proportionately effective for such insulation as the situation under discussion demands. The quality is one which may vary in degree and correspondingly in effectiveness of insulation. Owing to the persistent and searching action of chlorin in the presence of an electric current, even such a universally-accepted insulator as glass eventually disintegrates and permits the substances in solution in the apparatus to have access to the unprotected corrodible conductor. Experience with sundry insulating materials has demonstrated that ordinary precedents cannot be relied on where the selection of material for an insulator in connection with the process described in my patent aforesaid is concerned, and I have discovered that, unlike rubber and glass, vitrified porcelain is permanently reliable under the trying conditions which prevail in my process aforesaid, and therefore in the construction of electrode connections of whatever form I use this porcelain as the insulating material for the protection of corrodible conductors. Again referring to the form of electrode connections which involves the use of the pocket-shaped duct, I have found in practice that the platinum pin P can be strongly and securely sealed in the porcelain, where that is the material used, by inserting the pin in the porcelain before it is baked and then baking the pin into the porcelain, which in becoming vitrified fuses into close adhesive contact with the pin. Another form of porcelain which is vitrified, so as to furnish substantially the same effective qualities, is that which is termed "hot-cast" porcelain, in which the glaze element is more predominant than in the porcelain made in the usual manner.

What I claim, and desire to secure by Letters Patent, is—

1. The combination with the inclosing case of a cell for electrolytic or kindred purposes, of a plurality of introductory conduits for electrode connections each of the said conduits consisting of a tube of insulating material closed at one end, passing through the inclosing case and having its open end outside and its closed end inside the case, a pin on non-corrodible conducting material passing through and sealed in the inner end of the insulating-tube, and protruding from the wall of the tube both inside and outside, and having an electrical conductor in contact with the inner end of the pin and leading through the open end of the tube, and wires strung between the exposed ends of the several pins.

2. An introductory conduit for electrodes which consists of a tube of vitrified porcelain, closed at one end, a pin of platinum passing through and sealed in the closed end of the tube, a copper conductor within the tube, joined electrically to the intruding end of the platinum pin, and a filling of asphalt in the tube, inclosing the copper conductor.

3. An electrode and connections thereto which consist of a tube of insulating material

closed at one end, a pin of non-corrodible conducting material sealed in the closed end of the tube and protruding from and intruding within the tube, and an active electrode consisting of filaments of non-corrodible conducting material radiating from and supported by the protruding end of the pin.

4. As a new article of manufacture, an electrode connection consisting of a tube of vitrified porcelain, open at one end and closed at the other, having a pin of non-corrodible metal fused in the closed end so that the points of the pin protrude from and intrude within the tube.

Signed at Boston, Massachusetts, this 5th day of May, 1899.

HENRY CARMICHAEL.

Witnesses:

ROBERT CUSHMAN,

E. F. GROLL.