June 12, 1934. A. GEORGIEV 1,963,049

ELECTROLYTIC CELL AND PART THEREOF AND METHOD OF MAKING THE SAME

Filed Sept. 21, 1931

Fig. 1.

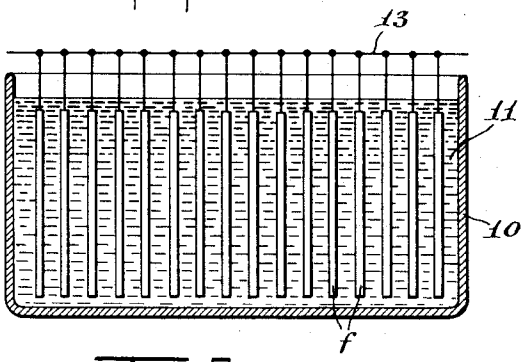


Fig. 2.

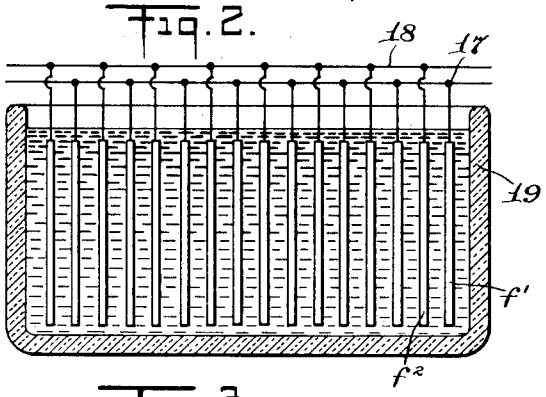


Fig. 3.

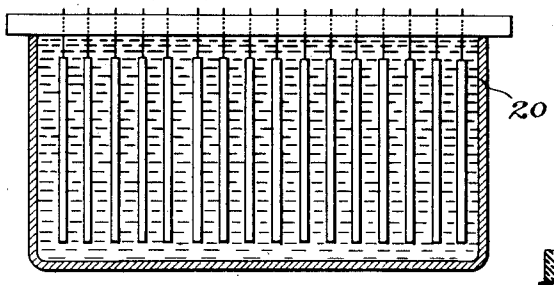


Fig. 4.

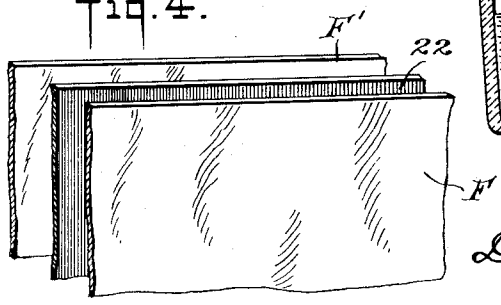


Fig. 5.

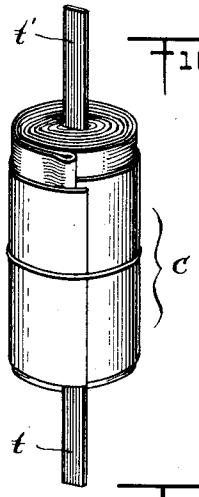


Fig. 6.

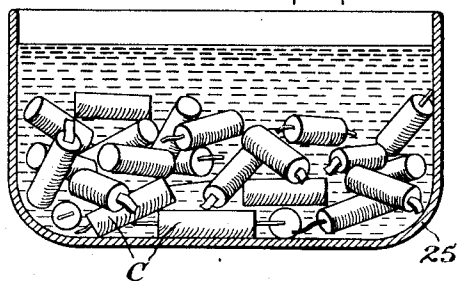
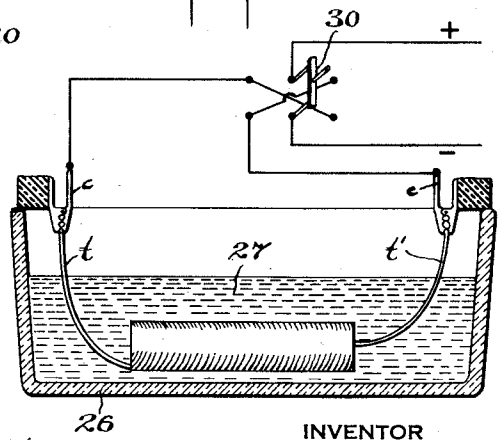


Fig. 7.



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ELECTROLYTIC CELL AND PART THEREOF AND METHOD OF MAKING THE SAME

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Application September 21, 1931, Serial No. 563,961

12 Claims. (Cl. 175—315)

My present invention relates to electrolytic cells more particularly to electrolytic condensers of the type useful in radio reception, in wire telephony and in power transmission, as for power factor compensation.

It is among the objects of the invention to provide an electrolytic condenser which, while still preserving the advantage of very high capacity in small bulk, will withstand a reversal of polarity without destruction of its efficacy and which is, therefore, well adapted for use on circuits involving such reversal either by accident or in regular course of normal operation.

Another object is to provide for the deliberate or accidental reversal of polarity in a condenser of the above type without departure from the construction of electrolytic condensers of otherwise approved design but that lack this characteristic.

Another object is to provide a method for expeditiously producing an electrolytic cell of the above type with the use of relatively simple equipment, and without the need for superlative care in supervision.

According to the invention, both electrodes or sets of electrodes, those used as the anode as well as those serving as the cathode, are pre-conditioned by appropriate treatment to pre-dispose them, for readily forming on either or both of them a di-electric film of great tenacity and permanence, such as greatly to resist deforming upon reversal of current.

The invention may be carried into execution according to one aspect thereof by forming only the anode, leaving the cathode in pre-conditioned state, so that upon reversal of current, the cathode would readily form, to build up the condenser for useful operation on such reversed polarity.

According to another aspect of the invention, both electrodes or sets of electrodes are formed with the thin di-electric film, so that the condenser structure is symmetrical and will operate without regard to which of the electrodes is used as the anode and which as the cathode.

According to another aspect of the invention, the forming of one of the electrodes is carried on to a greater degree than the forming of the other electrode, in which case satisfactory protection is afforded against reversal of polarity under relatively high voltage and yet the condenser is of capacity higher than where both electrodes are formed to equal degree.

The conditioning of the foils is preferably according to the method of the copending application of Samuel Siegel, Serial No. 535,180, filed May 5, 1931, but in the present case, the material of the foil not only for the anode, but also that for the cathode elements of the condenser is pre-treated.

While the invention is by no means limited thereto, it has its preferred application in electrolytic condenser structures of the general type disclosed and claimed in my prior Patent No. 1,789,949 of January 20, 1931, and while not limited to the use of that particular electrolyte, the invention brings about its best results when use is made in the condenser of the electrolyte disclosed and claimed in my prior Patent No. 1,815,768 of July 20, 1931.

In the accompanying drawing in which is shown one or more of various possible embodiments of the several features of the invention,

Fig. 1 is a diagrammatic view indicating the apparatus for pre-conditioning the material of the condenser foil,

Fig. 2 shows alternative apparatus for the pre-conditioning operation,

Fig. 3 is a diagrammatic view illustrating the washing operation,

Fig. 4 is a fragmentary perspective view indicating the correlation of the electrodes with each other in building up the condensers,

Fig. 5 is a perspective view indicating the general construction of the completed condenser roll,

Fig. 6 is a view in longitudinal cross-section illustrating the impregnation of the condenser units, and

Fig. 7 is a view in longitudinal cross-section showing the condenser forming operation.

Referring to Fig. 1 of the drawing, the foil from which all the electrode material of the cell is to be made, is immersed in a tank 10 which is charged with dilute sulphuric acid 11, and which could be of, or lined with a suitable metal. The foil (f) to be conditioned is immersed in the bath in said tank, and the electric feed line 13 is connected to said foils in parallel as anode the return being through the metallic wall 10 or lining of the tank which constitutes the cathode of said pre-conditioning cell.

If alternating conditioning current is used, the current is passed as shown in Fig. 2: between two foils or two sets of foils f^1 and f^2 connected to opposite sides of the electric line 17—18. In this case, the tank 19 should preferably be of some non-conducting material, such as stone, wood, hard rubber or the like.

In each case, the sulphuric acid bath is diluted

in water, which need not be distilled, ordinary tap water being found satisfactory. In practice a solution of 7 per cent to 35 per cent of sulphuric acid is suitable for the purpose and a good solution is obtained at ten per cent.

For direct current, about 20 volts is found satisfactory for the purpose and for alternating current about 20 volts R. M. S. may be applied, although lower and higher voltages are also practical. Under direct current the treatment is preferably for about fifteen minutes and under alternating current the time of treatment is approximately double. A current density of 5 to 30 amperes per square foot has proved suitable in practice. The temperature of the sulphuric acid during treatment should preferably be maintained below 85 degrees F., a temperature of about 55 degrees being found most advantageous.

After the material of the foils has been preconditioned in the manner just set forth, the foil racks are removed from the pre-treating tank and washed preferably as diagrammatically indicated in Fig. 3 by dipping in water in a tank 20, thereby to remove all traces of sulphuric acid and to leave on the foil a film which is the electro-chemical result of such sulphuric acid acting on the aluminum. Preferably the foil is dipped successively in a battery of washing tanks like that of Fig. 3 the contents of the final one of which is analyzed from time to time. Substantial purity of the water in said tank demonstrates the efficacy of the washing operation. The film formed by this electro-chemical treatment is more or less transparent, tough and makes a crackling sound when the apparently dry foil is bent near the ear, but the film does not appear noticeably to chip off.

The film produced in the preconditioning operation is designated in certain of the claims as "foundation film". It is electro-chemically formed as set forth preferably from an aqueous solution prior to incorporation of the foil in the condenser structure. The handling of the foil in rolling the condenser unit causes slight fissures in the foundation film, but any forming operation of the substantially non-aqueous electrolyte that is thereafter incorporated in the condenser structure promptly results in producing the final film satisfactory under all conditions of practical use, as will appear more fully hereinafter.

The foil material thus pre-conditioned and washed is now assembled into the condenser structure. As shown in Fig. 4, the cathode foil F and anode foil F' are superposed, preferably in staggered relation as shown, with an intervening layer 22 of gauze or other absorbent material separating the two electrodes. The superposed anode, cathode and intervening gauze are now rolled together, mechanically to complete the condenser structure C shown in Fig. 5, from the ends of which protrude terminal tabs *t* and *t'* respectively of the cathode and the anode.

A batch of the condenser rolls C is now immersed in the electrolyte tank 25 as shown in Fig. 6. The electrolyte 26 therein, preferably that disclosed and claimed in my prior Patent No. 1,815,768 comprises a mixture of glycerol borate and ammonium glycerol borate with appropriate quantities of water to bring the viscosity thereof between the limits of three and seven at 200 degrees F. as compared to water at 60 degrees F. Other electrolytes may be used with results corresponding to the relative efficacy of such electrolytes.

The electrolyte which is maintained heated in tank 25 readily soaks up into the gauze 22 of the respective condenser rolls C, whereupon these rolls are removed from tank 25 and placed in trays, such as shown in Fig. 7 for forming thereof. Each tray 26 has therein a quantity of electrolyte 27 identical with that in the impregnating tank 25 and accommodates four or five of the condenser rolls. The terminal tabs *t* and *t'* from the condenser rolls within each tray 26 are connected as shown, respectively to terminal clips *c* suspended from the rim of the tray and free from engagement with the electrolyte in the tray.

The forming current is now applied in the manner set forth more particularly in my prior Patent No. 1,789,949. The anode thereby is formed by electro-chemical action of the electrolyte thereon and the thickness of the di-electric film thus built up on the pre-conditioned film will depend on the length of treatment. A resistor unit (not shown) is disposed in series with the parallel-connected condensers in each tray, to keep down the initial voltage across the condenser, but as the film is formed and the resistance of the condenser to the flow of the forming current increases, the voltage drop across the condensers also increases. Thus, this forming operation is continued with automatic increase of the applied voltage across the terminals of the condenser and such forming is discontinued only when the voltage thus applied across the terminals exceeds somewhat the voltage under which the condenser is actually to be used. The forming operation with the use of the pre-conditioned foil as set forth, takes but a fraction of the time required for forming without such preconditioning. This period depends on the formation voltage and is greater for higher voltages. On 500 volts a period of fourteen hours or less is sufficient to complete the forming as compared to thirty or forty hours previously required.

In actual use of the condenser, with the anode formed on the pre-conditioned anode foil and the cathode merely pre-conditioned in the same way as the anode, but otherwise unformed the operation is particularly advantageous upon any current reversal whether accidental or intentional. The characteristic of the pre-conditioned foil by which its initial forming is expedited, appears largely to account for a relatively rapid building up of a di-electric film upon the cathode foil during actual use of the condenser with its polarity reversed. Thus, on reversed polarity, the cathode forms a di-electric film, while the anode film does not readily deform. As a consequence, the condenser will operate quite satisfactorily without breakdown on its reversed polarity, although the capacity will be somewhat reduced due to the presence now of a di-electric film, on each of the two electrodes.

As indicated in Fig. 7 a reversing switch 30 may be associated in the circuit connections 31 to the forming tray 26. According to another feature of the invention, after completion of the forming of the anode foil as above set forth, the switch 30 is thrown to reversed position and the forming current is now applied with reversed polarity. Under these conditions, the cathode is formed on the pre-conditioned cathode foil in the same way as the anode had previously been formed on the pre-conditioned anode foil. This forming operation may be continued until the voltage applied on the condenser with its polarity thus reversed is equal to the maximum voltage on which the anode foil had previously been formed. The resulting condenser will be an entirely symmetrical entity in which either terminal at will may be used as the anode with-

out difficulty. A condenser thus constructed could be installed in a radio receiving circuit for instance, without the need for the precaution heretofore necessary in connecting up to assure correctness of polarity. It would be particularly advantageous in radio sets to be operated from direct current outlets.

In the conventional formation of an alternating current electrolytic condenser by the use of alternating current, the ordinary industrial power lines are inadequate for the tremendous current consumption required, especially for high voltage condensers. Where instead of alternating current, direct current is applied in a succession of steps first in one direction and then in reverse direction, no appreciable impedance is imposed by the forming condenser, only ohmic resistance being developed, and, accordingly, the usual available power lines are adequate for the purpose, unless the voltage for which the condenser is to be prepared is in excess of the power line voltage, in which case, it can be readily stepped up to 500 volts or more by an ordinary motor generator set.

Obviously after completion of the formation of the anode, the forming may be conducted according to the present invention, so that the cathode foil has a di-electric film thereon, of lesser thickness than that of the anode foil, the result being thus intermediate between the two extreme conditions previously described. A condenser thus formed will have a higher capacity than a symmetrical condenser formed to equal degree on both electrodes and yet will afford effective protection on reversal of polarity even under relatively high operating voltages.

It will thus be seen that there are herein described apparatus and methods in which the several features of this invention are embodied, and which apparatus and methods in their action attain the various objects of the invention and are well suited to meet the requirements of practical use.

As many changes could be made in the above construction, and many apparently widely different embodiments of this invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:—

1. An electrolytic cell comprising cathode and anode foils, each having a coating thereon presenting comparatively low di-electric properties, but adapted to facilitate the electrolytic formation of a film of high di-electric properties, said cell having such film of high di-electric properties formed both on the anode and the cathode element thereof, the film on one of said elements being thicker than that on the other of said elements.

2. An electrolytic cell for direct current circuits comprising clean electrode elements both of aluminum, electrolyte medium interposed between the surfaces of said elements, said surfaces of said elements having a foundation film thereon of a compound of aluminum to facilitate the formation of a di-electric film on either of them under appropriate operating conditions, one of said electrodes having further di-electric film thereon, and the other electrode being substantially devoid of such further film.

3. An electrolytic cell for direct current circuits comprising closely juxtaposed clean electrode elements, interposed absorbent means, liquid electrolyte soaked therein, the surfaces of both electrode elements having a foundation film thereon of a compound of aluminum to facilitate formation of a di-electric film on either or both of them, one of said electrodes having further dielectric film thereon and the other electrode being substantially devoid of such further film.

4. An electrolytic cell for direct current circuits comprising electrode foil elements both sets of clean aluminum and closely juxtaposed, an absorbent interlay therebetween permeated with film-forming electrolyte, each of the surfaces engaged by said interlay being also chemically treated to form a foundation film on said surfaces of a compound of aluminum, thereby to facilitate the formation of a di-electric film thereon under appropriate operating conditions, one of said electrodes having further di-electric film thereon, and the other electrode being substantially devoid of such further film.

5. An electrolytic cell for direct current circuits comprising closely juxtaposed cathode and anode elements both of aluminum, film forming electrolyte interposed between said elements, the surfaces of both cathode and anode elements that are contacted by the electrolyte being chemically modified by electro-chemical pre-treatment in a sulphuric acid bath, the anode having further di-electric film thereon, and the cathode being substantially devoid of such further film.

6. An electrolytic cell comprising cathode and anode elements, both of aluminum and closely juxtaposed, the entire surface of said elements being of the product resulting from electro-chemical treatment thereof with sulphuric acid, liquid electrolyte maintained in a relatively thin film between said surfaces and a thin di-electric film of the type which constitutes the product of the reaction of such electrolyte upon such foil, said film in close adherent contact with the anode, the cathode being substantially devoid of any further film formed from said liquid electrolyte.

7. An electrolytic cell for direct current circuits comprising elongated strips of cathode and anode foils of film forming metal with interposed absorbent material, all wound into a coil, both the cathode and anode foils throughout their contiguous surfaces having a foundation film thereon of a compound of the metal of said foils for pre-disposition to facilitate formation, and a thin di-electric film on the anode foil and absent from the cathode foil.

8. An electrolytic cell comprising electrodes of aluminum, interposed absorbent material permeated with electrolyte, said electrodes having their contiguous surfaces of composition resulting from the electrolytic action of sulphuric acid thereon, the completed condenser having its anode and not its cathode modified by a thin di-electric film thereon resulting from the action of electric current on the condenser.

9. An electrolytic cell comprising electrodes of aluminum, interposed absorbent material permeated with electrolyte, said electrodes having their contiguous surfaces of composition resulting from the electrolytic action of sulphuric acid thereon, the completed condenser having its anode modified by a thin di-electric film thereon resulting from the action of electric current on the condenser and its cathode lacking such film.

10. An electrolytic cell comprising electrodes of aluminum foil, interposed absorbent material

permeated with electrolyte, said electrodes having their contiguous surfaces of composition resulting from the electrolytic action of sulphuric acid thereon, the completed condenser having both of its electrodes modified by a thin di-electric film thereon resulting from the action of electric current on the condenser, first with one of the electrodes as the cathode, and then the other of the electrodes as the cathode, the thicknesses of the di-electric films on the two electrodes being unequal.

11. The method of forming an electrolytic condenser for direct current circuits from electrodes of film forming metal which consists in producing a foundation film of a compound of said metal on all of the electrodes thereby to facilitate formation and to hinder deformation of further di-electric film thereon, and then forming solely the positive electrode of the completed condenser.

12. The method of forming an electrolytic condenser which consists in pretreating all of the electrodes to facilitate formation and to hinder deformation thereof and then forming the completed condenser first with current in one direction and then with current in reverse direction, but at different maximum voltages whereby the two electrodes are formed to different degree.

ALEXANDER GEORGIEV.