

# United States Patent

Icxi et al.

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[45] Jan. 25, 1972

[54] **ELECTRODES FOR ELECTROLYTIC PROCESSES**

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[22] Filed: **Apr. 25, 1969**

[21] Appl. No.: **819,142**

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[30] **Foreign Application Priority Data**

Apr. 29, 1969 France .....149897

[52] U.S. Cl. ....204/15, 204/143 R, 204/143 M, 204/224, 204/271, 204/274, 204/284

[51] Int. Cl. ....C23b 5/48, C23b 5/76

[58] Field of Search .....204/224, 271, 143 RM, 294, 204/286, 284, 15

[56] **References Cited**

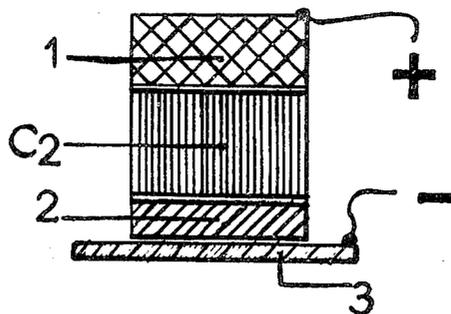
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[57] **ABSTRACT**

This invention relates to electrolytic electroplating processes and devices. In accordance with the invention, the absorbent material that is conventionally used, for example, in the brush or tampon process, consists of an absorbent porous carbon material. A device for use in this context can comprise an electrode in contact with at least one carbon material member.

**7 Claims, 11 Drawing Figures**



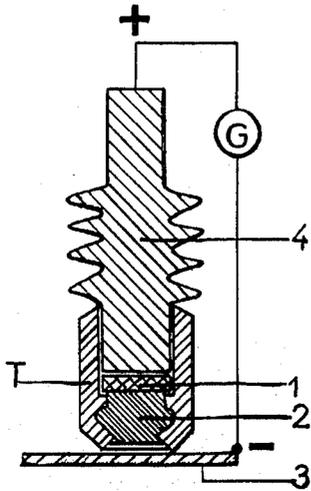


FIG 1  
PRIOR ART

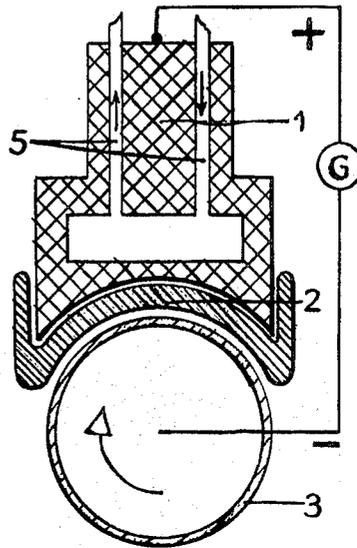


FIG 2  
PRIOR ART

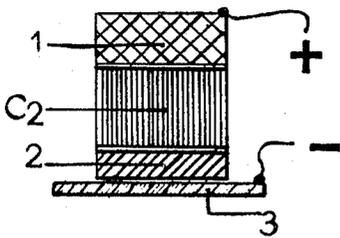


FIG 3

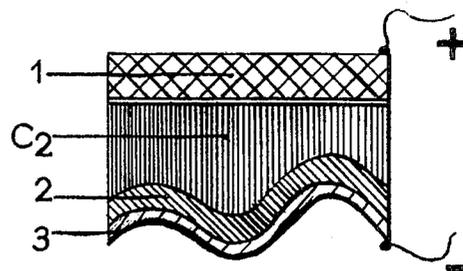


FIG 4

SHEET 2 OF 3

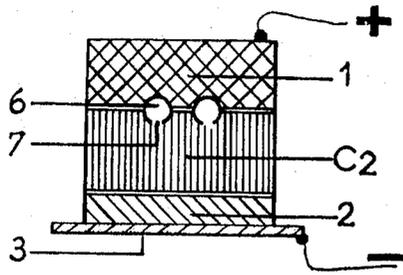


FIG 5

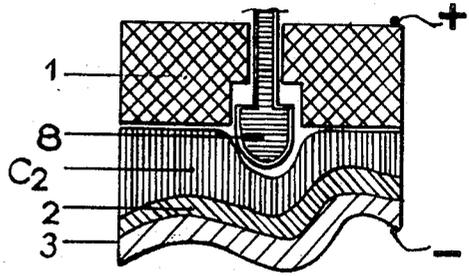


FIG 6

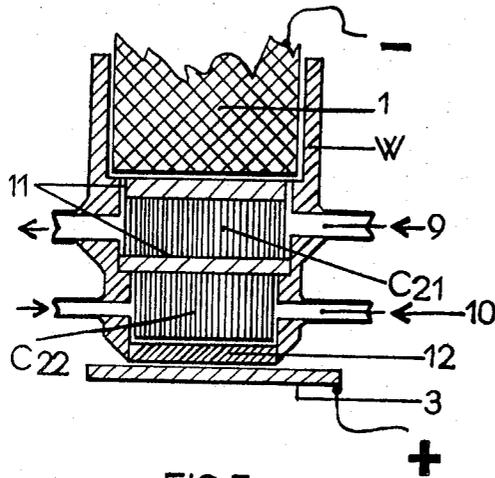


FIG 7

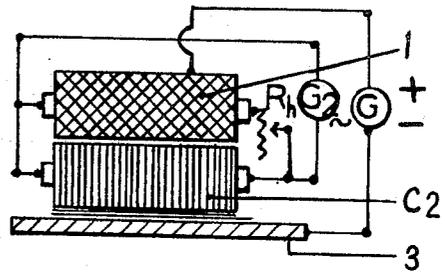
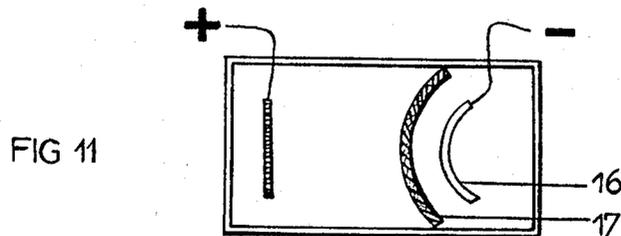
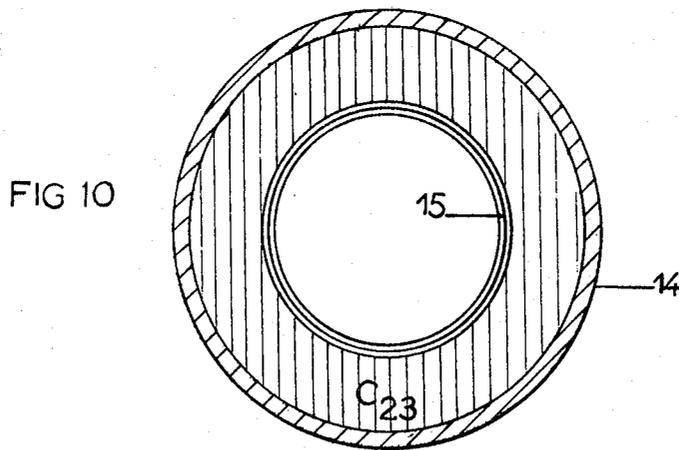
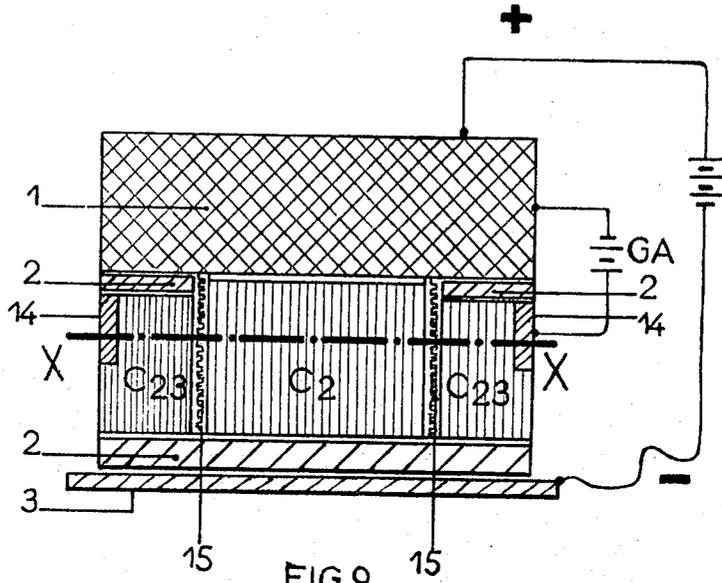


FIG 8



## ELECTRODES FOR ELECTROLYTIC PROCESSES

Electrolytic processes using brush and tampon, etc., are well known and have important industrial applications, not only in the fields of metal and metal-alloy depositions but also in the field of electrochemical treatments and applications, such as for example: anodic oxidation, electrochemical machining and/or polishing, etc. The characteristics are much the same whether the workpiece to be treated be the cathode or the anode. The process consists essentially in moving an absorbent device, impregnated with an appropriate electrolyte, on the conductive workpiece to be treated.

It is an object of the invention to obtain a substantially uniform electric field and to diminish the resistance of the absorbent material. It is also an object to be able to make the absorbent material as thin as possible.

To this end, the invention consists in an electrolytic process utilizing highly absorbent porous carbon materials, particularly in those processes known as brush or tampon processes, and is applicable both to anodic systems, e.g., for the deposition of metals, and to cathodic systems, e.g., for anodic oxidation, electrochemical machining and electrolytic polishing.

The invention also consists in a device useful to carry out this process, and comprising an electrode in contact with at least one carbon material member. The member is preferably nonrigid and may be cemented to the electrode with organic substances followed or not by pyrolysis. Alternatively, the parts may be attached to one another by threads which may or may not be, carbon.

These devices may be used in contact with electrodes, to receive electrolytic feeding; to serve as devices for the circulation of a fluid; to enable them to be heated by the same means or by an electric current, or to be polarized in relation to the electrode. They may also be used in electrolysis by means of fused salts. In tank plating processes they may be used to change the behavior of soluble anodes or to establish an homogeneous electric field or to improve electrodes used in electrochemical machining.

In order that the invention may be more clearly understood, reference will now be made to the accompanying drawings which show some embodiments thereof by way of example, and in which:

FIG. 1 shows a diagrammatic representation of the known electrodeposition of metals,

FIG. 2 schematically shows a known system of electrolytic plating with cooling,

FIG. 3 shows a first embodiment of a device according to the invention,

FIG. 4 shows how the distance between a pseudoanode and a cathode can remain constant,

FIG. 5 shows an anode with certain fittings,

FIG. 6 shows an insulating component,

FIG. 7 shows a means for the distribution of electrolytes,

FIG. 8 shows a device capable of receiving electrolysis of fused salts,

FIG. 9 shows a device comprising a protecting ring,

FIG. 10 shows a cross section along the line X—X of FIG. 9, and

FIG. 11 schematically shows how a substantially uniform electric field is obtained.

Referring now to the drawings, in the case of the known electrodeposition of metals, FIG. 1 shows an anode 1 in contact with an absorbent material 2 that is rendered electrically conductive by impregnating it with an appropriate electrolyte, the constituent materials of the tampon being preferably hydrophilous cotton-wool, cellulose, etc., or hydrophobic synthetic fabrics, brushes with nonconductive bristles, etc., or a combination of these. The whole of the anode 1 and the absorbent material 2 is contained in an electrically nonconductive head T. The anode 1 and a workpiece 3 to be plated forming the cathode are, of course, connected to an electric power source schematically illustrated at G. This device may use either soluble anodes (e.g., copper in the case of electrodeposition of copper), or alternatively nonsoluble anodes.

The use of a high-current density necessary for industrial applications of the process requires a higher voltage than that used for conventional bath plating which results in the production of heat by the Joule effect, and therefore often requires the cooling of the plating device. This is obtained either by an air-cooled metallic radiator 4 as shown in FIG. 1 or by the circulation of a fluid 5 (e.g., water) as shown in FIG. 2. FIG. 2 represents schematically the plating of a rotating, cylindrical-shaped workpiece component 3, a water jacket in which the cooling fluid 5 circulates being incorporated in the anode 1.

In order to obtain a uniform electric field and to diminish the electrical resistance of the absorbent material 2 the thickness of the latter is to be as thin as possible (see example in FIG. 2). The absorbent power of this material is therefore reduced and the circulation of the electrolyte which occasionally is injected, consequently becomes more difficult.

The applicants have solved these difficulties by using self electrically conductive absorbent materials described as porous material of amorphous or graphitized carbon obtained for instance by pyrogenation of organic (natural or synthetic) felts, fibers, cloth, etc.

FIG. 3 shows a device which illustrates in principle the object of the present invention. The anode 1 is put into contact with a porous carbon material member C2 placed in between the anode 1 and the nonconductive absorbent material 2. These carbon materials (amorphous or graphitized) may absorb for example an amount of electrolyte equal to 90 percent of their proper volume. Considering that their own electric conductivity is far superior to that of the impregnating electrolyte, for example about 90 percent of the current passing through the device may thus be conducted by this porous material. Consequently, one may use a voluminous absorbent material C2 and 2. The thickness of the nonconductive absorbent material 2 may be reduced since the carbonaceous material C2 serves as an anode and is therefore in close contact with the surface of the workpiece 3 to be treated. For this reason the electric field is much more homogeneous, the coating more even, the Joule effect reduced, all of which represents an important advantage.

Moreover, this absorbent material is nonrigid and adaptable to any complex shaped profiles without requiring any specific machining of the anode 1; since the easily adaptable, conductive carbonaceous absorbent part operates as an anode, the distance between this pseudoanode and the cathode remains constant (FIG. 4).

The intrinsic electrical conductivity of the material of the member C2 makes it easy to provide the anode 1 with different fittings e.g., perforated electrolyte tubes 6 made of insulating materials 7 as shown in FIG. 5; mechanically or otherwise deformable anodes, even by an insulating component 8 as shown in FIG. 6, since the electric current is distributed by the carbonaceous material C2 underneath this insulator and therefore maintains a uniform electric field without any blanketing effect.

These porous carbon materials are very suitable for the manufacture of complicated assemblies. By the use of organic cements they may be attached together or to carbon or graphite supports or other materials with a basic carbon content. The assemblies thus obtained may subsequently be heat treated, i.e., pyrogenized or pyrolyzed as a result of which an entirely carbonaceous matter is obtained.

This makes it possible to place tubes inside the absorbent material 2 to provide for the circulation of heating or cooling fluids 9 and for the distribution of the electrolytes 10 as shown in FIG. 7 where the absorbent material is made of two graphite plates 11 fixed to a porous carbonaceous material C21 and to another porous carbonaceous material C22—the whole assembly being contained in an electrode 1 support W allowing at C21 the distribution of a fluid with thermal action and at C22 electrolyte distribution—and of a nonconductive porous material 12 e.g., asbestos.

The chemical inertia of the absorbent carbon materials allows for the use of electrolytes such as those containing con-

centrated sulphuric or phosphoric base acid which normally cannot be used with nonpyrolyzed absorbent organic materials.

The device of FIG. 7 can be adapted for electrolytic polishing, the workpiece 3 becoming the anode and the electrode 1 becoming the cathode.

These carbon materials are not destroyed by high temperatures, and are thus suitable for use in a device capable of receiving electrolysis of fused salts as shown in FIG. 8 where a high temperature supplied by a low-voltage AC current G2 is transmitted via a rheostat Rh, to the anode 1 and a carbon ring C2 insulated from the workpiece 3 cathode and the anode 1.

They can further be used to change the current distribution by appropriate polarization. The diagram of FIG. 9 shows a device comprising a protecting ring C23. This ring is made of a graphite tube 14 fixed and pyrogenated onto a ring C23 of porous carbon material and is subsequently polarized in relation to the anode 1 by an auxiliary power source GA for example. The protecting ring is insulated by an insulating liner 15 from the porous absorbent material C2 in contact with the anode 1 and is placed inside the noncarbonaceous absorbent mass 2. FIG. 10 shows a cross section along the line X—X of FIG. 9 of the different components of this protecting ring C23.

Insoluble anodes are often sensitive to electrolytic reaction and are subject to wear in the long run. The use of conductive absorbent material acting more or less as an anode as shown in FIG. 3 protects the insoluble anodes from this type of wear. An accidental short circuit between the carbonaceous material and the workpiece is temporary and without danger since the contact, being perfectly wet, prevents sudden current rises.

In the case of a soluble anode clad with the material forming the subject of the present invention, the material reduces the dissolution of the anode, for example: with an appropriate thickness of the carbonaceous material the rate of dissolution of the anode may be kept equal to the rate of deposition on the cathode in case the latter is inferior to the former. For conventional plating applications in tanks, anodes clad with one of these materials that may also serve as a filter for the residues from the anode dissolution, maintain the stability of the bath plating solutions. In placing the porous carbon material 17 close to the cathode 16 a uniform electric field is achieved and provided that its thickness is small the material does not act as an intermediate electrode since due to its porous texture any metallic deposit is avoided as shown in FIG. 11.

This is the same in the case of electrochemical treatments in tanks where the workpieces to be treated become anodes such as for example in electrochemical polishing, etc. The cathodes may thus be protected against electrolytic attacks, etc.

Particularly in the case of electrochemical machining without a tampon, cathodes modified according to the present invention represent a considerable advantage. As is well known, electrochemical machining consists essentially in an electrolytic attack of the anodic part with a suitable electrolyte by means of an insoluble cathode having a shape similar to that of the part to be machined. For this purpose, a very small gap between anode and cathode (approx. 20/100 mm. in most cases) is absolutely necessary to ensure an electric field as uniform as possible and to allow the highest current densities, a rapidly flowing electrolyte being passed into the gap. Since the cross section of the electrolyte flow is very small, the electrolyte must be injected under high pressure requiring strong supports able to resist heavy mechanical stresses and to ensure a precise positioning of the anode and cathode.

The applicants have found that a cathode clad with a porous amorphous or graphitized carbon material, due to its permeability during the electrolyte flow (e.g., 90 percent of its proper volume) makes it possible to increase considerably the speed of the electrolyte flow (e.g., 200 times) and to reduce in an even greater proportion the pressure required for the electrolyte circulation while still maintaining a very small gap owing to the fact that the porous carbon material acts partially

or totally as an electrode due to its very high electric conductivity. Consequently, it is easier to provide the supports and it is even possible to operate in open tanks as used for conventional electrolytic treatments, thus reducing the danger of explosive gas mixtures, the detrimental rise or variation of temperature, the danger of accidental short circuits, etc.

The manufacture of these improved cathodes is carried out as described above for other types of electrodes by assembling, forming, cementing sometimes followed by pyrolysis, etc., to obtain the desired shapes. The very small gap between the porous carbon material and the workpiece to be treated plays the part of the nonconductive porous material holding the electrolyte in the processes known as brush or tampon plating processes.

It will be understood that the devices shown in FIGS. 5, 6, 7 and 9 are also applicable for electrodes used for electrochemical machining without tampons as well as for other electrochemical treatments in tanks where such type of electrodes provide a solution to the high current density conditions and forced electrolyte circulation.

The following indicative, but not restrictive examples will ensure better understanding of the advantages of the present invention.

#### EXAMPLE I

A prior art device such as that shown in FIG. 1 with a certain electrolyte solution gives the following characteristics:

voltage under load	16 v.
current density	200 A./dm. <sup>2</sup>

with a thickness of 12 mm. for a nonconductive tampon.

The same device, modified as shown in FIG. 3 which is one of the embodiments of the present invention with the same electrolyte solution, the tampon being made of a 3 mm. nonconductive material 2 and a 9 mm. amorphous carbon felt C2 leads to the following new conditions:

voltage under load	10 v.
current density	200 A./dm. <sup>2</sup>
Joule effect reduced	by 40%

#### EXAMPLE II

Copper plating of a cylinder with an electrolyte consisting mainly of copper sulphate and sulphuric acid using a prior art device as shown in FIG. 2 at a current density of 40 A/dm.<sup>2</sup> results in a wear of the graphite anode 1 at a rate of 10 mm./h.

With an intermediate absorbent material C2 according to FIG. 3 having a thickness of 17 mm. the wear of the graphite anode is reduced to 1.5 mm./h.

#### EXAMPLE III

With a device as shown in FIG. 2 for the coating of an aluminum piston 500 mm. in diameter, 600 mm. in length and of an average thickness of 25 mm., the current passing through the nonconductive tampon 2 and the piston 3 has to be kept down to 300 a. because of the danger of overheating due to the flow of current. If a higher current density is applied the plating has no longer the required physical properties, and might not adhere to the base metal owing to the latter's expansion.

The introduction of a system such as shown in FIG. 7

thickness of C21	17 mm.
thickness of C22	9 mm.

placed in between the anode 1 and the nonconductive absorbent material 12 permits the use of a current density of 750 a. thus increasing by 2.5 times the normal plating speed.

EXAMPLE IV

Using a device as shown in FIG. 1 the anodic oxidation of aluminum with a sulphuric acid solution 200 g./l. at 12 v. has become possible by replacing the nonconductive absorbent 2 with a chemically inert tampon made of:

17 mm. of graphitized carbon absorbent C2

1 mm. of P.T.F.E. fine-mesh fabric (0.07 mm. thread)

according to the principle shown in FIG. 3 except that the polarities are reversed.

We claim:

1. A process for the electrolytic treatment of a conductive workpiece, wherein said workpiece is held in contact with one face of a constant thickness layer of a nonconductive absorbent material, the opposite face of said layer is held in contact with one face of a layer of highly absorbent flexible electrically conductive material of fibrous porous carbon permanently filled with electrolyte, the opposite face of said carbon layer is held in contact with a conductive electrode element, the workpiece is connected to one pole of an electrical power source, and the electrode element is connected to the other pole of said power source.

2. An electrode assembly for the electrolytic treatment of a conductive workpiece comprising an electrode layer element

connectable to one terminal of an electrical power source, an electrically conductive layer of a highly absorbent flexible fibrous carbon in contact with said electrode layer, and a layer of porous nonconductive material in contact over one face thereof with said carbon layer and adapted, while remaining of constant thickness, to be held with its opposite face in contact with the workpiece which is to be treated and which is connectable to the other terminal of said power source.

3. An electrode assembly according to claim 2, wherein the electrode is provided with perforated tubes of insulating material for transporting the electrolyte.

4. An electrode assembly according to claim 2, wherein the absorbent carbon layer is provided with tubes for the circulation of heat exchange fluid and for the distribution of electrolyte.

5. An electrode assembly according to claim 2, wherein the carbon layer is mainly graphitized carbon.

6. An electrode assembly as claimed in claim 2, wherein the assembly is cemented together with organic cements.

7. An electrode assembly as claimed in claim 6, wherein the cemented assembly is pyrolyzed with carbonaceous electrodes.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,637,468 Dated January 25, 1972

Inventor(s) JEAN J. G. ICXI and PHILIPPE J. TILCHE

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

[30] Foreign Application Priority Data

April 29, 1968 France 149897

Signed and sealed this 9th day of January 1973.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents