

PATENT SPECIFICATION

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- (21, Application No. 30782/72 (22) Filed 30 June 1972 (19)
 (23) Complete Specification filed 29 June 1973
 (44) Complete Specification published 3 March 1976
 (51) INT. CL.² C25C 7/02 1/20
 (52) Index at acceptance
 C7B A2A1 A2A2 A2B1 A2C2 A2C3 A2C4X A3
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(54) ELECTRODE FOR METAL RECOVERY

(71) We, KODAK LIMITED, a Company registered under the law of England, of Kodak House, Station Road, Hemel Hempstead, Hertfordshire, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an electrode for the recovery of metals from solutions containing metal ions.

In general, cells for the recovery of metals comprise a container for the solution containing metal ions which form the electrolyte. A pair (at least) of electrodes is located in the container in such a position as to be immersed in the electrolyte in use. One of the electrodes is arranged to be the cathode and the other is arranged to be the anode of the cell. The constitution of the electrodes depends on the nature of the electrolyte and the metal to be recovered. In use, a D.C. potential from a suitable source is applied across the electrodes and the metal ions are caused to migrate to the cathode where they are discharged and converted to metal atoms which generally adhere to the cathode. When sufficient metal has deposited on the cathode it is usually taken from the cell and the deposit removed therefrom, after which the cathode is replaced in the cell. The cell may be arranged to operate in a batchwise manner in which case electrolysis is continued until the concentration of metal ions in the cell is reduced to a predetermined level at which point the electrolysis is discontinued and the depleted solution replaced by a fresh solution. Alternatively, the cell may be arranged to operate in a continuous manner in which case the electrolyte is passed through the cell from an inlet to an outlet at a predetermined rate. The rate of passage of the electrolyte through the cell is such that a satisfactory proportion of the metal ions in the solution are discharged and converted to metal atoms at the cathode.

According to the present invention there is provided a combustible electrode suitable for use in the electrolytic recovery of metals

from solutions, which comprises carbon fibres, as the electrically-conducting material, and a solution-permeable support therefor formed of a combustible material.

An electrode of the invention may be incinerated after use as a cathode to facilitate recovery of metal deposited thereon.

An electrode of the invention may conveniently form part of an assembly of two or more electrodes, and such an assembly preferably comprises a housing which surrounds the electrodes, each electrode having an electrical terminal which extends through a wall of the housing. In a preferred form of construction, the housing, each electrode, and each electrical terminal, is combustible so that after use the whole assembly may be incinerated without any prior dismantling.

An electrode assembly comprising a housing may have a perforated housing arranged for insertion into an electrolyte container. Alternatively, it may be made liquid tight so that a separate electrolyte container is not needed, in which instance the electrode assembly constitutes an electrolytic cell. In either case, the electrode assembly is a self-contained unit which may be supplied ready for insertion into a metal recovery apparatus. When sufficient metal has been deposited on the cathode, the unit can be removed from the recovery apparatus and a further unit inserted therein.

A combustible electrode, or electrode assembly, of the present invention is particularly useful for the recovery of silver from used photographic fixer solutions.

Generally, carbon fibre is in the form of graphitic threads formed by the heat-treatment of organic polymers such as polyacrylonitrile. One such commercially available material is "Grafil" (Trade Mark) sold by Courtaulds Limited in the form of a tow of 5000 to 10000 filaments of 8-9 microns mean diameter. Each "Grafil" filament has a resistance of about 400 ohms per cm. An equivalent carbon fibre is made by Hercules Powder Company under the trade name "MagnaMite". This fibre has the same filament diameter and resistance as the "Grafil" fibre described above.

Conveniently, the electrode may be made by sandwiching a layer of carbon fibre tow between two layers of a solution-permeable material which form the support. Preferably, the solution permeable material is an open-mesh material such as a wet-strong non-woven fabric, for example, tea-bag paper or paper towelling such as "J-cloth" (Trade Mark) sold by Johnson and Johnson Limited. Preferably, the two layers of fabric are stitched together to provide for convenient handling. The layers of solution-permeable material may be held on a frame of combustible material to make the electrode more rigid.

Alternatively, a solution-impermeable substrate, such as a sheet of a plastics material (for instance a cellulosic material or polyethylene terephthalate) may be provided with a layer of a solution-permeable binder holding the carbon fibres.

The carbon fibre may be used in the form of a felt containing fibres of other material such as textile material, e.g., cotton, nylon or polyester, as reinforcement. Alternatively, the tow may be spread out on the support and used in this form. In this case, it is preferred that there be substantial interlacing of the fibres to form an electrically conductive network. If the fibrous material felted with the carbon fibre is self-supporting, no additional support is required.

Preferably a pigtail of bunched carbon fibre tow is provided at one end of the electrode to enable an electrical connection to be made to the carbon fibre layer.

It has been found that a cell according to the present invention can be used to recover silver from an ammonium-type photographic fixer containing more than 1 gram per litre of silver at currents of up to 30 amps per square metre without the need for any agitation of the electrolyte. However, at concentrations below 1 gram per litre of silver there is a danger of sulphiding taking place unless the electrolyte is agitated or the current reduced.

An electrode assembly of the present invention can be made in a wide variety of configurations. Where the assembly is in the form of a self-contained unit enclosing the electrodes and the housing is liquid-tight, it may have an inlet and an outlet arranged to be connected up to a solution supply and a drain respectively.

In the alternative case where the housing enclosing the electrodes is in the form of a perforated cartridge arranged for insertion into an electrolyte container forming part of the metal recovery apparatus, the perforations are preferably made small enough to prevent an operator being able to interfere with the electrodes. Conveniently, the housing is surrounded by an open-mesh material such as tea-bag paper which retains any

metal particles which may fall from the cathode for example when the cartridge is being replaced.

A housing can take many forms. For example, it can be in the form of a cylinder. It may contain a single anode and a single cathode in the form of open-ended concentric cylinders or sheets convoluted together particularly where the housing is in the form of a cylinder. In the case where the electrodes are in the form of convoluted sheets having a plastics material solution-impermeable substrate, the cathode would have an electrically conductive layer on both of its surfaces. Preferably, in this embodiment of the invention the cathode would be perforated to enable the silver deposited on the two surfaces to become bonded together. Similarly, the anode would have an electrically conductive layer on both sides. Alternatively, the substrate could be in the form of a perforated sheet with the electrically conductive layer on one side thereof.

Further, a plurality of flat anodes and cathodes can be interdigitated in substantially parallel relationship to one another or the cell can contain a single anode and a single cathode in opposed relationship to one another.

In another embodiment of the present invention, one or more combustible cathodes of the invention can be used in a cell which contains one or more anodes arranged to remain in the cell when the cathodes are removed and replaced.

The life of an electrolytic cell according to the present invention which is, or comprises, a self-contained unit can be defined in terms of the number of amp-hours required to yield a satisfactory deposit of silver. Alternatively, the cell can be run until enough metal accumulates to short-circuit the electrodes. In this case means could be provided to switch off the apparatus in response to any of the changes of cell characteristics which occur. Alternatively, visual or audible alarm means could be provided to indicate when this has taken place.

The present invention will now be described further by way of example, with reference to the accompanying drawing, in which:—

Fig. 1 is a partially broken away, perspective view of an electrode assembly according to the present invention; and

Fig. 2 is a perspective view of an electrolytic cell according to the present invention arranged to be inserted into a tank of electrolyte such as a used fixing solution in a metal recovery apparatus;

Fig. 3 is a perspective view showing another embodiment of the electrolytic cell, having provision for passing a flowing stream of electrolyte through the cell.

In Fig. 1 there is shown an electrode

assembly 10 having four electrodes 11 which can be assigned at will to anodic or cathodic roles and connected or interconnected accordingly so that each electrode is a counter electrode for its next adjacent electrode or electrodes. In use, the assembly is located within a housing 21, shown in phantom, to form a self-contained unit as will be described more fully herein after.

Each electrode 11 comprises a light but fairly rigid hollow plastics frame 12 which serves to extend and support a double thickness of an open-mesh material such as 'J-cloth', which forms a support 13, including, as the electrically conductive material, a layer of carbon fibre tow 14. The layer of carbon fibre tow 14 has been spread out to substantially cover the area of the support 13 bounded by the frame 12. The two layers of the support are tacked together in a few places, by means not shown, to hold the spread of fibres substantially in place.

The open mesh material of support 13 of each electrode contains a plurality of holes 17, only some of which are shown, but which extend across its whole area.

The electrodes 11 are arranged to be supported and located with respect to each other by means of plastics rods 15, with at least the lower ones resting in saddles 18 in the housing 21. Each of the carbon fibre tow layers is formed into a pigtail 16 or 16' of different signs at one end which forms an electrical terminal in use. The positive pig-tails are joined at a terminal 25, and the negative pigtails are joined at a terminal 25', both terminals being connected to a battery or other source of direct current B.

In Fig. 2 there is shown an electrolytic cell 20 in the form of an immersible self-contained unit having a housing 21 containing an electrode assembly such as that shown in Fig. 1 as described above, and arranged to be inserted in an electrolyte container 26, shown in phantom, of a recovery vessel. The housing 21 has a handle 24 and contains perforations 22 around its sides, but not on the bottom. Only some of the perforations 22 are shown. The perforations 22 are such as to allow free access of electrolyte by convection when the unit is immersed therein while restraining manual interference with the electrode assembly. Although the bottom is not perforated it can conveniently have a hole to allow solution to drain away when the spent unit is lifted from a recovery tank (not shown) containing electrolyte. The level to which the unit is arranged to be immersed is shown by a broken line 23. The line 23 is at a safe level below a pair of electrical contacts 25, 25' of different signs and is defined by the height of the overflow from the recovery vessel with which the cell is to be used. It is important that free emergence of the electrolyte from the housing

through the perforations 22 be allowed at this level since in the case where the electrolyte is used photographic fixer, for example, the desilvered solution rises to the top by convection.

Preferably, the electrolyte container 26 with which the unit is intended to be used is a rectangular vessel a little larger in internal dimensions than the unit.

In use, the electrolyte is admitted at or is led to or is allowed to reach the bottom of the vessel without deliberate intermixing with the solution already in the vessel. The electrolyte demetallised at the cathodes rises by convection and is drained from the recovery vessel at the height of the surface at a point far from the inlet. For convenience, a handle 24 is provided to enable the unit to be inserted into and removed from the recovery vessel easily.

In an alternative embodiment of the present invention shown in Fig. 3, the housing 21' of the electrolytic cell is sealed and liquid-tight, and has a handle 24'. In use electrolyte is led into and out of the unit by access pipes, an inlet pipe 28 leading to the bottom and an outlet pipe 30 being located at the desired level of the surface of the electrolyte.

WHAT WE CLAIM IS:—

1. A combustible electrode suitable for use in the electrolytic recovery of metals from solutions which comprises carbon fibres, as the electrically-conducting material, and a solution-permeable support therefor formed of a combustible material.
2. An electrode according to claim 1 wherein the support comprises a layer of a solution-permeable binder which holds the carbon fibres and is coated on a solution-impermeable substrate.
3. An electrode according to claim 1 wherein the support comprises an open-mesh material.
4. An electrode according to claim 3 wherein the support comprises two sheets of the open-mesh material between which the carbon fibres are sandwiched.
5. An electrode according to claim 3 or 4 wherein the open-mesh material is a wet-strong non-woven fabric.
6. An electrode according to any of claims 3 to 5 wherein the support comprises a frame of a combustible material to which the open-mesh material is attached.
7. An electrode according to any of the preceding claims wherein the carbon fibres are bunched together at one end to allow electrical connection to be made thereto.
8. An electrode according to claim 1 wherein the support for the carbon fibres comprises fibres of the combustible material, the two kinds of fibres being felted together.
9. An electrode substantially as described

assembly 10 having four electrodes 11 which can be assigned at will to anodic or cathodic roles and connected or interconnected accordingly so that each electrode is a counter electrode for its next adjacent electrode or electrodes. In use, the assembly is located within a housing 21, shown in phantom, to form a self-contained unit as will be described more fully herein after.

Each electrode 11 comprises a light but fairly rigid hollow plastics frame 12 which serves to extend and support a double thickness of an open-mesh material such as 'J-cloth', which forms a support 13, including, as the electrically conductive material, a layer of carbon fibre tow 14. The layer of carbon fibre tow 14 has been spread out to substantially cover the area of the support 13 bounded by the frame 12. The two layers of the support are tacked together in a few places, by means not shown, to hold the spread of fibres substantially in place.

The open mesh material of support 13 of each electrode contains a plurality of holes 17, only some of which are shown, but which extend across its whole area.

The electrodes 11 are arranged to be supported and located with respect to each other by means of plastics rods 15, with at least the lower ones resting in saddles 18 in the housing 21. Each of the carbon fibre tow layers is formed into a pigtail 16 or 16' of different signs at one end which forms an electrical terminal in use. The positive pig-tails are joined at a terminal 25, and the negative pigtails are joined at a terminal 25', both terminals being connected to a battery or other source of direct current B.

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through the perforations 22 be allowed at this level since in the case where the electrolyte is used photographic fixer, for example, the desilvered solution rises to the top by convection.

Preferably, the electrolyte container 26 with which the unit is intended to be used is a rectangular vessel a little larger in internal dimensions than the unit.

In use, the electrolyte is admitted at or is led to or is allowed to reach the bottom of the vessel without deliberate intermixing with the solution already in the vessel. The electrolyte demetallised at the cathodes rises by convection and is drained from the recovery vessel at the height of the surface at a point far from the inlet. For convenience, a handle 24 is provided to enable the unit to be inserted into and removed from the recovery vessel easily.

In an alternative embodiment of the present invention shown in Fig. 3, the housing 21' of the electrolytic cell is sealed and liquid-tight, and has a handle 24'. In use electrolyte is led into and out of the unit by access pipes, an inlet pipe 28 leading to the bottom and an outlet pipe 30 being located at the desired level of the surface of the electrolyte.

WHAT WE CLAIM IS:—

1. A combustible electrode suitable for use in the electrolytic recovery of metals from solutions which comprises carbon fibres, as the electrically-conducting material, and a solution-permeable support therefor formed of a combustible material.
2. An electrode according to claim 1 wherein the support comprises a layer of a solution-permeable binder which holds the carbon fibres and is coated on a solution-impermeable substrate.
3. An electrode according to claim 1 wherein the support comprises an open-mesh material.
4. An electrode according to claim 3 wherein the support comprises two sheets of the open-mesh material between which the carbon fibres are sandwiched.
5. An electrode according to claim 3 or 4 wherein the open-mesh material is a wet-strong non-woven fabric.
6. An electrode according to any of claims 3 to 5 wherein the support comprises a frame of a combustible material to which the open-mesh material is attached.
7. An electrode according to any of the preceding claims wherein the carbon fibres are bunched together at one end to allow electrical connection to be made thereto.
8. An electrode according to claim 1 wherein the support for the carbon fibres comprises fibres of the combustible material, the two kinds of fibres being felted together.
9. An electrode substantially as described



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herein with reference to Figure 1 of the accompanying drawings.

10. An electrode assembly which comprises at least two electrodes at least one of which is according to any of the preceding claims.

11. An electrode assembly according to claim 10 which comprises a housing which surrounds the electrodes, each electrode having an electrical terminal which extends through the wall of the housing.

12. An electrode assembly according to claim 11 wherein the housing, each electrode, and each electrical terminal, is combustible.

13. An electrode assembly according to claim 11 or 12 wherein the housing is perforated and is arranged for insertion into an electrolyte container.

14. An electrode assembly according to claim 11 or 12 wherein the housing is liquid-tight and is provided with an inlet and outlet for solution to be electrolysed.

15. An electrode assembly according to claim 13 substantially as described herein with reference to Figure 2 of the accompanying drawings.

16. An electrode assembly according to claim 14 substantially as described herein with reference to Figure 3 of the accompanying drawings.

17. An electrolytic cell which comprises an electrolyte container, an anode and a cathode, at least the cathode being an electrode as specified by any of claims 1 to 9.

18. An electrolytic cell which comprises an electrolyte container and an electrode assembly as specified by any of claims 10 to 13.

19. A method of recovering a metal from a solution containing a compound thereof which comprises electrolysing the solution in an electrolytic cell according to claim 17.

20. A method according to claim 19 wherein, after electrolysis has been effected, the cathode is incinerated.

21. A method of recovering a metal from a solution thereof which comprises electrolysing the solution in an electrolytic cell according to claim 18 or in an electrode assembly according to claim 14.

22. A method according to claim 21 wherein, after electrolysis has been effected the electrode assembly is incinerated.

23. A method according to any of claims 19 to 22 of recovering silver from a used photographic fixing solution.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1976.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY
from which copies may be obtained.



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