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PATENT SPECIFICATION

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(54) METHOD FOR THE ELECTROCHEMICAL PROCESSING OF METAL SURFACES

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Republic of Germany, a Body Corporate
organised according to the laws of the
Federal Republic of Germany, 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 invention relates to the
electrochemical processing of metal
surfaces of workpieces.

A method of electrochemical processing
has been proposed in our U.K.
Specification 1,407,425 in which the
processing is carried out with the
workpiece contacted by electrolyte of an
electrolytic cell but not in contact with
either the anode or the cathode of the cell.
For the removal of metals, charge must of
course be supplied to the workpiece, and
for transporting this charge from the anode
to the surface of the workpieces being
processed electrically conductive material
is suspended in the electrolyte. For this
material there is suggested either graphite
powder or particles of insulating material
coated with a metal layer. This material is
prevented from discharging at the cathode
by a diaphragm shielding the cathode.

Printed circuits can be produced by this
method from plastics material plates which
are laminated with copper on one or both
sides. After applying a protective layer to
mask those parts of the metal surfaces
which are to form the printed circuit the
remainder of the copper lamination is
removed electrochemically. The
electrically conductive material suspended
in the electrolyte is charged positively at
the anode of the electrolysis cell and then
together with the electrolyte is brought into
contact with the surface of the copper
layer; copper ions go into solution from this
layer, and these are deposited again at the

cathode of the electrolytic cell. The method
can also be used for the production of metal
profiles where it is important to achieve
high precision and sharp contours, for
example in flow-conducting parts such as
turbine blades or nozzles or for producing
surface relief on printing plates or
cylinders.

The direct recovery of the removed
metal is possible since this is deposited on
the counter-electrode. This can provide an
economical method of manufacture, and
can avoid the release of waste metal to the
environment.

This method of electrochemical
processing can also be utilised for the
recovery of metals from so-called cable
scrap. In this case the workpiece is
constituted by the cable scrap.

As was mentioned above, particles either
of graphite or of insulating material coated
with a metal layer have been suggested as
the conductive material suspended in the
electrolyte. Both of these have good
electrical conductivity; but a disadvantage
of both is their relatively small surface area,
which limits the amount of electrical charge
which can be transported per part by
weight of suspended material. A
consequence of this, in some cases, is that the
method is not sufficiently economical.

According to the present invention there
is provided a method for electrochemically
processing a metal surface of a workpiece
wherein the workpiece is out of contact
with anode or cathode of the cell, and the
surface to be processed is contacted by
electrolyte of or from an electrode-
containing region of the cell which
electrolyte has electrically conductive
material suspended therein for transporting
charge from the electrode to the surface,
the or each electrode of opposite polarity
being shielded by a diaphragm which
prevents the said conductive material from
reaching and being discharged at a said
electrode of opposite polarity, and electric
current is passed through the cell,

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characterised in that at least part of the said conductive material suspended in the electrolyte is provided by activated carbon powder which has been heat treated at a temperature of at least 700°C in an inert atmosphere.

The workpiece surface may be exposed to the electrolyte within a region of the cell, or may be exposed to the electrolyte in a chamber separate from the cell, and to which electrolyte containing charged conductive material is circulated, for example as disclosed in our U.K. Specification 1,407,425.

It has been found that activated carbon powder heat treated as specified above not only has a very large specific surface but is also so suitable for transporting electrical charge that when such activated carbon powder is suspended in the electrolyte there can be a reduction in the quantity of conductive material required in the electrolyte for a given quantity of metal to be dissolved and/or there can be a considerable acceleration in the removal of the metal layers with a consequent reduction in processing time. The heat treatment of the activated carbon powder in an inert atmosphere is preferably carried out in a nitrogen atmosphere or under a vacuum. Air and water vapour need not be excluded provided that the amount of them is sufficiently small that the surface of the activated carbon is attacked chemically to only a relatively slight extent. Preferably activated carbon powder is used which has been heated to a temperature in the range 900°C to 1200°C for at least one hour.

In a further development of the invention graphite powder is used as part of the electrically conductive material in addition to the activated carbon powder and in this connection attention is drawn to the claims of our U.K. Patent 1,407,425. As a result it is possible (and is advantageous) to raise the potential difference between the metal surface being treated and the suspended particles of electrically conductive material, and the method can be made more economical. The good electrical conductivity of the graphite particles is combined with the high ability of the particles of activated carbon to store charge for the removal of metal from the surface of the workpiece.

The invention will now be explained further with reference to the accompanying drawings, in which:—

Figure 1 is a vertical cross-section of apparatus used for carrying out both the method of the invention and also comparisons in which other conductive materials were suspended in the electrolyte;

Figure 2 is a graph in which the current

transmission I is plotted against the potential difference ΔE between the conductive particles suspended in the electrolyte and the metal surface being treated; and

Figure 3 is a graph in which the stored charge quantity Q (which can be used for metal dissolution) per gram of suspended particles is plotted against the potential difference ΔE between the suspended particles and the metal surface to be treated;

Figures 2 and 3 show curves (III) for particles of heat treated activated charcoal in accordance with the invention, and as a comparison curves for particles of graphite and of commercial activated charcoal (curves I and II respectively).

As Figure 1 shows, the apparatus for carrying out the method comprises an electrolytic cell 1 with anode 2 and cathode 3. Between the electrodes of the electrolytic cell 1 there is situated a diaphragm 4 which divides the electrolysis cell 1 into two chambers or cell regions. The cell region 5 containing the anode 2 also contains the workpiece 8. There is no electrical connection between the workpiece 8 and any electrode — either anode or cathode — of the electrolytic cell 1.

In this region 5 of the cell, particles of electrically conductive material are suspended in the electrolyte. The particles are charged electrically at the anode 2. The diaphragm 4 prevents the electrically conductive particles from passing into the region 6 of the electrolytic cell. This region 6 contains the cathode 3 of the cell and thus the diaphragm 4 functions to prevent discharge of the suspended particles at the cathode.

In this embodiment, the anode 2 is rotated by an electric motor 7, and by its rotation it is able to stir the electrolyte in the electrolytic cell and cause movement such that electrolyte with positively charged suspended particles is brought into contact with the surface of the workpiece 8 which is to be treated. The circulation of the electrolyte is indicated by arrows.

At the surface of the workpiece 8, the positively charged suspended particles give up their charge, and an electrochemically equivalent amount of metal ions go into solution in the electrolyte. In this embodiment the workpiece has a copper surface; copper ions go into solution, these pass through the diaphragm 4 and are deposited as copper metal on the cathode 3 of the electrolytic cell 1. The discharged suspended particles are carried back to the anode 2 as the electrolyte moves, charged once again at the anode, and cycled back to the workpiece 8.

Example 1 (Comparative)

20 g of commercially obtainable activated carbon powder was suspended in 150 cm³ of dilute sulphuric acid adjusted to 0.5 normal and positively charged in the anode chamber 5 of the electrolytic cell, with intensive stirring. The activated carbon particles were prevented from discharge by the diaphragm 4 which was impervious to the activated carbon particles.

Coulometric measurements in the electrolytic cell gave, for a potential difference ΔE between the activated carbon particles and the metal surface of the workpiece, the charge quantity Q storable by the particles suspended in the electrolyte and which could be transported to the metal surface.

For a potential difference $\Delta E = +0.7V$ the charge quantity Q was found to be 75 coulombs per gram of activated carbon powder. Therefore, per gram of copper to be dissolved, 40 g of activated carbon powder were required to be brought into contact with the metal surface.

Charge transfer between the particles suspended in the electrolyte and the metal surface being treated was measured potentiostatically. Instead of a workpiece to be treated, a third electrode acting as a discharge electrode with a surface of 15 cm² was brought into contact with the electrolyte in the cell region 5. The electrode was set to the electrical potential of copper, which corresponds to a voltage of +0.34V against a standard hydrogen electrode. The transmitted current I was measured in the case of a potential difference ΔE between the activated carbon particles and the discharge electrode of $\Delta E = +0.6V$. During measurement, the anode 2 had a speed of revolution of 400 r.p.m. Maintaining these conditions, 60 mA was transmitted, corresponding to a rate of dissolution of copper of 1.18 mg per minute.

Example 2

20 g of activated carbon powder which in accordance with the invention had been heat treated for one hour at 1000°C under a nitrogen atmosphere was put in suspension in 150 cm³ of dilute sulphuric acid adjusted to 0.5 normal, and positively charged in the same way as in Example 1. For a charge quantity Q to be stored and capable of being transmitted to the metal surface, a value of 125 coulomb per gram of activated carbon powder was measured for a potential difference between the activated carbon particles and the metal surface being treated of $\Delta E = +0.7V$. Therefore, per gram of copper to be dissolved 24 g of activated carbon powder were required to

be brought into contact with the metal surface.

The charge transport was ascertained in the same way as in Example 1. Under the same conditions, the transmitted current amounted to 360 mA, corresponding to a dissolution of copper surface at the rate of 7.1 mg per minute.

Figure 2 provides a comparison of results obtained with different conductive materials suspended in the electrolyte. The comparison is between graphite powder, commercially obtainable activated carbon powder, and activated carbon powder which had been subjected to heat treatment at 1000°C for an hour in an inert (nitrogen) atmosphere. It is apparent that when using the activated carbon powder heat treated in an inert atmosphere (curve III) the charge transport in the range of potential difference ΔE up to 0.66V was increased both relatively to that when using graphite powder particles suspended in the electrolyte (curve I) and also relatively to that when using conventional commercial activated carbon powder (curve II). With an electrolyte containing the activated carbon powder particles heat treated in an inert atmosphere (curve III) roughly four times the current I could be transmitted with a potential difference ΔE of 0.6V. In Figure 3 there is plotted the charge quantity Q , storable by means of the particles suspended in the electrolyte, for the range of a potential difference of up to $\Delta E = +0.66V$. The curve designations correspond to those of Figure 2, namely curve I is for graphite powder as the conductive material suspended in the electrolyte; curve II is for conventional commercial activated carbon powder; and curve III is for activated carbon powder heat treated in an inert atmosphere.

The storable charge quantity Q per gram of electrically conductive material suspended in the electrolyte was greatest when using the heat treated activated carbon powder. Therefore, per gram of metal to be dissolved, the quantity of particles required to be brought into contact with the surface being treated was smallest when using the heat treated activated carbon powder.

Similar results were found when using activated carbon powder which had been heat treated for an hour at 700, 800 or 900°C in an inert gas atmosphere. However, the best results were obtained with heat treatment temperatures between 900 and 1200°C.

Example 3

In 150 cm³ of dilute sulphuric acid adjusted to 0.5 normal there was suspended 20 g of activated carbon powder which in

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accordance with the invention had been heat treated for an hour. This was positively charged in the same way as in Example 1 or 2. When charging with a current of 50 mA, after 20 hours a potential difference of $\Delta E = +0.9V$ was obtained between the activated carbon powder and a copper surface. Subsequently there was additionally put in suspension in the electrolyte 1 g. of graphite powder, corresponding to 5% of the total quantity of electrically conductive material added to the electrolyte. With the same current of 50 mA, after an hour the potential difference rose by 0.07V to 0.97V, that is to say by 8%. If greater additions of graphite were made, the attainable potential difference rose further.

WHAT WE CLAIM IS:—

20 1. A method for electrochemically processing a metal surface of a workpiece wherein the workpiece is out of contact with anode or cathode of the cell, and the surface to be processed is contacted by
25 electrolyte of or from an electrode-containing region of the cell which electrolyte has electrically conductive material suspended therein for transporting charge from the electrode to the surface,
30 the or each electrode of opposite polarity being shielded by a diaphragm which prevents the said conductive material from reaching and being discharged at a said electrode of opposite polarity, and electric
35 current is passed through the cell, characterised in that at least part of the said conductive material suspended in the

electrolyte is provided by activated carbon powder which has been heat treated at a temperature of at least 700°C in an inert atmosphere.

2. A method according to Claim 1, wherein the diaphragm divides the cell into an anode region and a cathode region, the surface being processed being immersed in the electrolyte in one of these regions, the electrolyte in this region having the conductive material suspended therein.

3. A method according to Claim 1 or Claim 2, wherein the activated carbon powder which is used is powder which has been heated to a temperature in the range 900°C to 1200°C for at least 1 hour.

4. A method according to Claim 1, Claim 2 or Claim 3, wherein graphite powder is used as part of the electrically conductive material in addition to the activated carbon powder.

5. A method according to any one of the preceding claims, wherein an electrode in the region of the cell which contains the workpiece is rotated to stir the electrolyte in that region.

6. A method according to Claim 1 for the electrochemical processing of metal surfaces of workpieces substantially as herein described with reference to Figure 1 of the drawings and as exemplified in Example 2 or Example 3 herein.

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WHAT WE CLAIM IS:—

1. A method for electrochemically processing a metal surface of a workpiece wherein the workpiece is out of contact with anode or cathode of the cell, and the surface to be processed is contacted by electrolyte of or from an electrode-containing region of the cell which electrolyte has electrically conductive material suspended therein for transporting charge from the electrode to the surface, the or each electrode of opposite polarity being shielded by a diaphragm which prevents the said conductive material from reaching and being discharged at a said electrode of opposite polarity, and electric current is passed through the cell, characterised in that at least part of the said conductive material suspended in the

electrolyte is provided by activated carbon powder which has been heat treated at a temperature of at least 700°C in an inert atmosphere.

2. A method according to Claim 1, wherein the diaphragm divides the cell into an anode region and a cathode region, the surface being processed being immersed in the electrolyte in one of these regions, the electrolyte in this region having the conductive material suspended therein.

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