TN's work for ~~Dick~~ BROWN.
— patent law project

MAR 7 - 1970

MAR 11 1970

Name
1st Notice MAR 1 1970
2nd Notice
Return

MR. THEODOR H. NELSON
458 West 20th Street
New York, New York 10011

93

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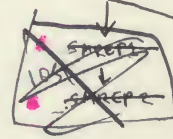# OVERALL LAYOUT OF LEGAL HYPERTEXT

• means text of this is in packet

• ~~PATENT~~ [header for whole file, short remark]

§ EXPL
[short explanation of
this demo & materials]

• ~~CNTNTS~~ [another level of contents]

• ~~ORDOCA~~
[original documentos:
menu of permuted lists
of abstracts]

• ~~LNKREP~~ [linked reports]

~~SPREP1~~
LDR
~~SPREPB~~

~~Other~~ New
linked documents,
to be kludged on
Tuesday night

[Identical lists
diffly. permuted]

• ~~ORDOCE~~
[~~by author~~]

ABSTRACTS
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[Abstracts headed &
permuted
by inventor]

• ~~ORDOCF~~
[Abstracts
headed &
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by title]

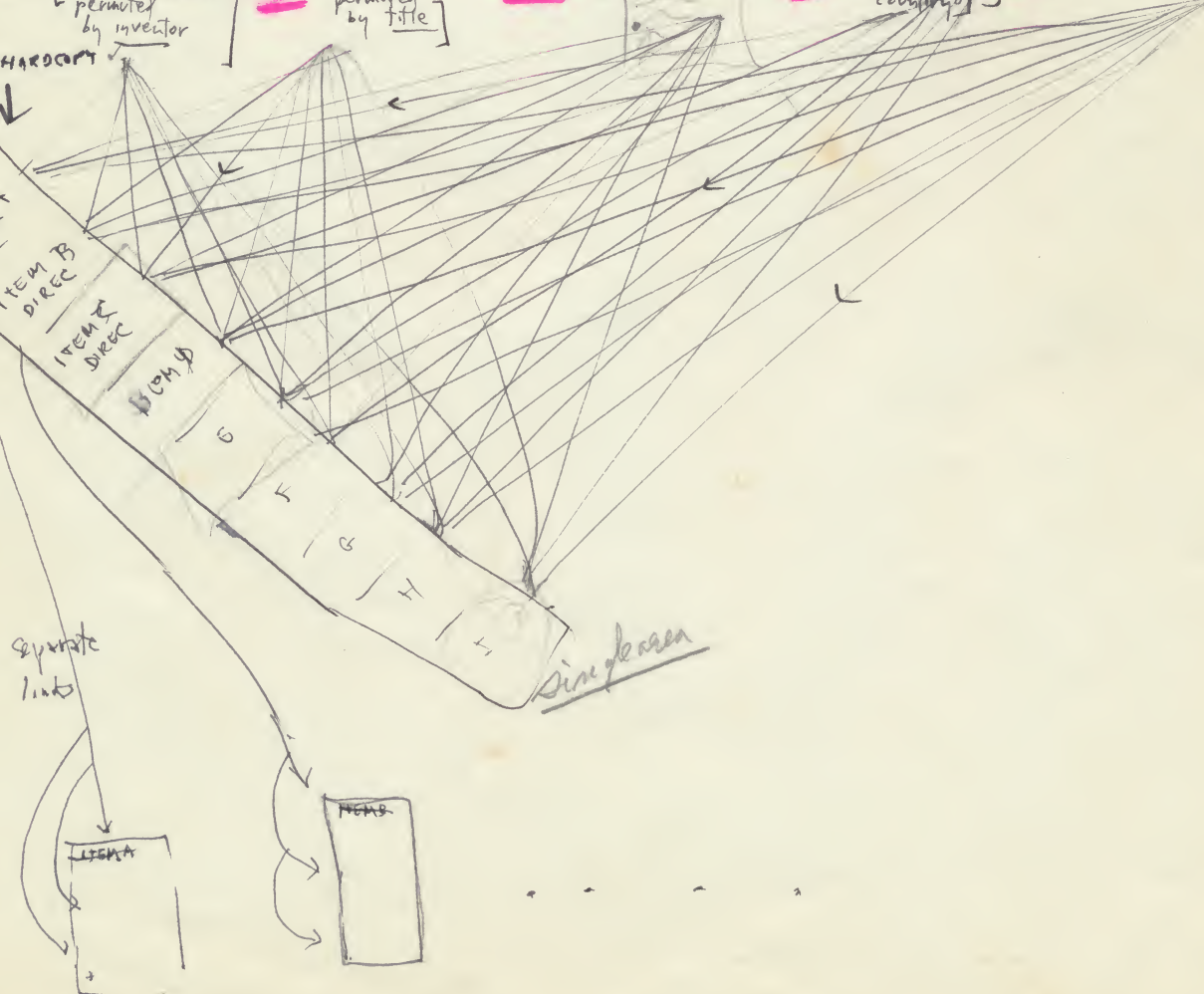~~ORDOCG~~
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and
country]

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[" by date of filing]

LINKS ↓
TO
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ITEM A
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I

ITEM = PATENT

single area

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FULL
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OF
ITEMS

ITEM A

ITEM B

NEW OR MODIFIED

LNKREP

~~REPORTS~~

REPORTS AND COMMENTS

LET US SAY,
THIS SECTION IS, DEVOTED TO REPORTS AND COMMENTS
BY THE LEGAL AND RESEARCH STAFF.

THE EXTRAORDINARY ADVANTAGE IS THAT ANY ~~FOR~~
QUOTE FROM A DOCUMENT MAY LINK DIRECTLY TO
THE OCCURRENCE WITHIN THE DOCUMENT ITSELF, AND ANY
COMMENTS ABOUT A DOCUMENT MAY LINK DIRECTLY
TO THE ~~APPROPRIATE~~ PARTS REFERRED TO.

~~ON ELECTRODES,~~
~~[SAMPA]~~ ✱ SAMPLE REPORT ~~SHORT~~ VERSION
~~ON ELECTRODES,~~
~~[SAMP2]~~ ✱ SAMPLE REPORT, SOMEWHAT LONGER VERSION
~~✱ LISTS~~
~~[FICT]~~ ✱ FICTITIOUS COMMENTS BY LEGAL STAFF

✱
✱
✱   } {Branch table of the different reports, by title}
✱   LDOC1
✱   LDOC2
✱   LDOC3
           LDOC4
           SMITH
           JONES

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                                    text
              later deleted batches of text.

cant make SAMPLE1

~~EXPL~~

THIS DEMONSTRATION IS INTENDED TO SHOW

THE USEFULNESS AND POWER OF THE INTERLINKED DOCUMENT,
OR HYPERTEXT, WHICH MAY BE STORED AND PRESENTED ON
THE HYPERTEXT SYSTEM.

THE DOCUMENTS WE ARE USING ARE PATENTS —
VARIOUS ~~PATENTS~~ ON MULTILAYER ELECTRODES WHICH
FEATURE CROSS-REFERENCING.

~~EACH~~
WE HAVE STORED VARIOUS CONVENTIONAL DOCUMENTS
~~WE HAS~~

WITHIN THE SYSTEM, AND COUPLED THEM TOGETHER
TO FORM A LARGER HYPERTEXT. ANY LINK-MARK
(*) SIGNIFIES A POSSIBLE JUMP TO CONNECTED

MATERIAL. ~~BY THE~~ BY USING THESE LINKS EDITORIALLY,
A MASS OF WRITING MAY BE CREATED
~~IN WHICH THE READER~~
IN WHICH THE READER HAS INSTANTANEOUS ACCESS
~~TO A VAST BODY~~ TO A VAST BODY OF MATERIAL,
IN WAYS MAKING IT CLEARER THAN USUAL.

THE DOCUMENTS WE ARE USING ARE PATENTS.
WE HAVE PUT IN THE FULL TEXT OF SEVERAL PATENTS
ON MULTILAYER ELECTRODES, AND SOME RELATED
MATERIAL.

RIGHT! THAT WAS A LINK. NOW GO ON BACK.

YOU MAY READ ANY OF THESE PATENTS ON THE SCREEN.

WHERE ONE OF THESE DOCUMENTS CITES ANOTHER, IT HAS A LINK-MARK (*).

~~YOU MAY GO AMONG ALL~~
YOU MAY JUMP TO A RELATED TEXT AT ANY TIME BY POINTING AT AN ASTERISK, AND ~~RETURN~~ PRESSING THE LINK BUTTON. AFTER READING IN THE RELATED TEXT YOU MAY IF DESIRED RETURN BY PRESSING ~~RE~~ THE RETURN BUTTON.

~~[* * * * * * * *]~~

DOSSIER ON ~~DISCUSSION OF~~ MULTILAYER ELECTRODES, ESP. TITANIUM

BY THE STAFF

We have in this dossier several patents and one article. We will here summarize and discuss these materials.

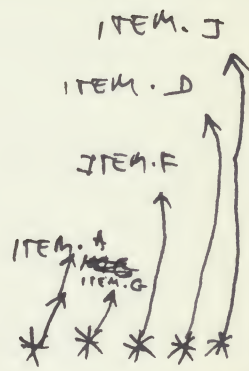There is a separate running essay which explains the terminology and ~~work~~ basic ~~te~~ technicalties in this area, ~~Very~~ ~~will and is linked as ~~*~~~~ and has running explanations and commentaries on each document. * ⟶
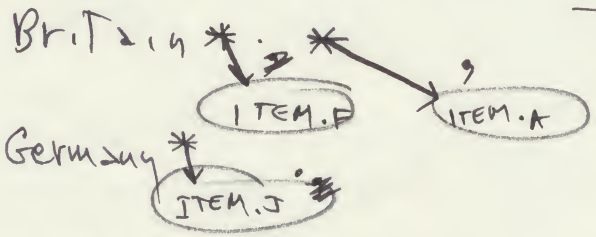
ITEM. J

ITEM. D

ITEM. F

ITEM. A
ITEM. G

→ The patents of Beer and his company * * * * *

~~cover~~

are concerned with three-layer electrodes,

having a titanium core, ~~then coating of~~
a noble metal (df*) jacket, and a "barrier layer"
between them ~~which~~ of titanium oxide.
This barrier layer is resistant to attack
by the ~~electro~~lyte (df*) is re-forming
in case of damage, and conducts electricity
well to the noble metal jacket.
Substantially similar patents making these claims are filed for
the United States * → ITEM. D ,
Britain * • *
ITEM. F   ITEM. A
and Germany *
ITEM. J

~~All of these~~
→ ITEM. G
A Canadian patent *
stresses the process of making the electrodes, especially
the creation of the oxide layer before the jacketing
in noble metal.

*By "noble metal" is meant any metal of the
platinum family: platinum, ruthenium, rhodium,
palladium, osmium, iridium and gold.

*the solution through which
electricity is being passed.

The Messner patent* is specifically related to chlorine. It covers a titanium or tantalum electrode with a platinum coat.

The patent by Chemische Fabrik Weissenstein* is paradoxical. It covers ~~#~~ tantalum electrodes which are only partly covered with platinum. This is ~~related to~~ related to per compounds.

The patent by Mueller* relates to an electrode of silver/copper/aluminum coated with tantalum and perhaps platinum. Possibly with a wire wound around it.

The patent by Burnham* is not for an electrode, but for a capacitive plate.

~~However, # uses in one embodiment #~~

However, it uses the same film-forming processes involved in the Beer patents.*

The article by Hall and Hackerman* covers fundamental research in the electrochemical processes relevant to this area, particularly the mechanisms of film formation.

on electrodes.

Their findings:

The nature and spread of the oxide film on Titanium is not well understood. It is hypothesized by some to be chemically absorbed oxygen. *
↓

L1
(page ~~262~~ 262, ITEM. I)

by others to be a true oxide layer. Hall and Hackerman believe these are both present, but the spread of the latter affects the former. *
↓

L3, p. 269, item. I

the irregularities in the speed of electrode charging have to do with the sequence of surface film changes. *
↓

L2
ITEM. I
page 264

~~\# \# \# \# \# \# \# \# \#~~

~~TECHEX~~ EXPLANATION OF TECHNICALITIES AND TERMS
ON MULTILAYER ELECTRODES
~~FOR~~

Electrodes are metal sticks or pieces
which carry electricity into a medium,
the medium may be either liquid ~~(an electrolyt~~
(such as a ~~lighting~~ plating bath) ~~bath~~ or solid (such
~~as a prisoner~~ as a prisoner being electrocuted).
~~Since electricity is said to~~ ~~Electrons flow from a negat~~

~~For the present purposes~~
~~electrodes are pieces of metal that~~
Two electrodes are needed to make current flow,
a negative and a positive.
~~If there is a voltage difference between~~
Electrons flow from the ~~more~~ negative pole
to the ~~more~~ positive.

~~The~~
Electrodes are useful for breaking up

chemicals (such as water), or ~~otherwise~~ chemicals contributing to the formation of ~~compounds~~ (such as ~~the~~ per compounds).

Such electrodes are generally eaten away ~~The the~~ in use. They dissolve, ~~the~~ or they become pitted; ~~the~~ thus the solution becomes tainted by them, or they shrink and lose efficiency.

Thus durable electrodes are desirable. However, the durability may reduce electrical efficiency.

~~Platinum~~

~~The patents by Beer ...~~

~~The patents~~

~~Comments~~

(Very simple-minded explanations of the different patents could follow here, to be linked into.)

~~LODES~~
LODES

MEMORANDA ~~WHAT SHALL WE DO ABOUT THE~~
ON ~~HE~~ MULTILAYER ELECTRODE PATENTS

~~19 MAY 1972~~

                LITTLE
TO: THE ~~BIG~~ BOSS
            BIG
FROM: THE ~~LITTLE~~ BOSS
19 MAY 1972

WHAT'S THE SITUATION ON MULTILAYER ELECTRODES?

TO: THE BIG BOSS
FROM: THE LITTLE BOSS
20 MAY 1972

I'LL HAVE ~~THE~~ JONES DRAW YOU UP A REPORT.

JONES

~~TO: THE LITTLE B~~

(JONES REPORT* ~~F~~ FILED AND CIRCULATED 23 MAY 1972)

TO: THE LITTLE BOSS
FROM: THE BIG BOSS
25 MAY 1972

PRETTY GOOD REPORT. DOES ANYONE DISAGREE?

TO: THE BIG BOSS
FROM: THE LITTLE BOSS
26 MAY 1972

YOUNG SMITH SEEMS TO. I'LL
HAVE HIM DRAW UP A DISSENTING VIEW.

{ BIG & LITTLE
~~SHD HEAD~~
HEADERS
OMITTED
HEREAFTER
BUT BELONG IN. }

{ TO LITTLE
~~2~~ 1 JUNE }

    FINE, FINE. I LIKE TO ENCOURAGE
INDEPENDENCE.

~~TO BIG~~
~~3 JUNE~~

SMITH

(SMITH REPORT* FILED AND CIRCULATED
3 JUNE 1972)

{ TO LITTLE
8 JUNE }

    SAY NOW. THAT BOY HAS SOMETHING.
DON'T ASK ME WHAT.

{ TO BIG
9 ~~8~~ JUNE }

    WHAT SHOULD WE DO?

{ TO LITTLE
9 JUNE }
    SUE!

{ TO BIG
9 JUNE }
    SUE WHO?

~~JONES~~

COMPLETENESS IN THE ELECTRODE PATENTS
BY R. JONES
23 MAY ~~15 JUNE~~ 1972

IT IS MY LEGAL OPINION THAT
BEER'S PATENT SETUP IS VERY CLEVER
AND COMPREHENSIVE.

~~HERE ARE THE~~

IN THE U.S. PATENT, FOR INSTANCE,
HE PATENTS THE THREE-LAYER ELECTRODE *,

↓

ITEM.D
CLAIM 1

WITH VARIOUS PRODUCTION TECHNIQUES,
~~INVOLVING SUCH TECHNIQUES~~
SUCH AS PAINTING ON THE BARRIER LAYER, *

↓

~~AN~~
ENTRY-POINT A
IN ITEM.D
CLAIMS

BURNING OFF SOLVENTS AND THE USE
OF REDUCING ATMOSPHERES, *

↓

ENTRY-POINT B
IN ITEM D
CLAIMS

AND ANODIC FORMING BY IMPRESSED VOLTAGE. *

↓

ENTRY-POINT C
IN ITEM D
CLAIMS

THE BEER PATENT STRUCTURE IS
~~ITS~~ MAGNIFICENT AND IMPREGNABLE,
IN MY HUMBLE OPINION.

~~#~~

LOOPHOLES IN THE ELECTRODE PATENTS
BY   J. SMITH

I   THINK THERE ARE WIDE LOOPHOLES   IN THE

BEER ELECTRODE PATENTS. * * * * *
                          ITEM.S
                          ITEM.O
                          ITEM.F
                          ITEM.G
                          ITEM.A

WHILE HE CLAIMS MAKING THE OXIDE LAYER
BEFORE THE NOBLE METAL JACKETING, * (E.G. *) .
                                            ↓
                                         ITEM.G
                                         CLAIM 1

AND   AFTER THE JACKETING (E.G. *).
                               ↓
                            ITEM.F
                            CLAIM 2

HOWEVER, THERE ARE NO CLAIMS ON
MAKING THE OXIDE LAYER ~~SIMULTANE~~
AT THE SAME TIME THE JACKET IS MADE.
MY BROTHER THE CHEMIST SAYS THIS WOULD BE EASY.
·I ADVOCATE INFRINGEMENT.

FURTHER INPUTS

Claims on ITEM.D

~~ITEM.G~~

ITEM.G Claims

ITEM. I

PINK-MARKED PARTS

p. 262,
264,
267.

Type instructions:

Label
Stars
Paragraphing

Don't type in any asterisks
except for long strings of islans

DAS 1,217,345

Case No. 114650 VIb/12h

Filing Date: April 2, 1958

Publication Date: May 26, 1966

METHOD FOR THE PRODUCTION OF AN ANODE FOR ELECTROLYSES OF
ELECTROLYTES CONTAINING CHLORINE-IONS

Applicant: Amalgamated Curacao Patents Co. N.V. Willemstad,
              Curacao (Dutch Antilles)

Agents: Dr. G. W. Lotterhos and Dr.-Ing. H. W. Lotterhos,
              Patent Attorneys, Frankfurt/M., Annastr. 19

Inventor: Henri Bernard Beer, Den Haag

Priority Claimed: Netherlands of April 9, 1957 (216,199)

For carrying out electrolyses on a technical scale, par-
ticularly in aggressive media, for example, the electrolysis
of alkali-metal chlorides, graphite anodes are usually used.
Since graphite anodes require a relatively large space, have
a low breaking resistance, and are subject to great wear, it
has been tried for some time to use mechanically and chemically
resistant metal anodes. Good results can be obtained with
electrodes of noble metals, particularly of platinum metals,
but these are economically not feasible because of the high
cost.

Electrodes are already known which consist of a core of
a base metal which is covered with a thin top coat of a noble
metal applied for example, by electroplating. Since such a

thin top coat always has pores through which the electrolyte
and aggressive anode products resp. can get to the core metal,
so-called filmforming metals must be used for the core anode,
that is, metals which form under electrolytic conditions on
their surface an inert, corrosion-resisting blocking film for
example, in the form of oxides.

It was found that titanium is particularly suitable as a
core metal if chlorine is formed on the anode in the nascent
state. For these cases it was found that other film-forming
metals, like tantalum, zirconium, bismuth, are completely un-
suitable in continuous operation. On the other hand, it could
not be expected on the basis of the known chemical as well as
electrochemical properties that titanium in particular could
be superior, compared to tantalum or zirconium.

The subject of the invention is a method for the production
of an anode for electrolyses of aqueous or molten electrolytes
containing chlorine-ions, consisting of a core of a base metal
and a porous top coat of noble metal, where the core is provided
electrolytically with a blocking film at the areas where the top
coat is porous. The invention is characterized by the fact that
titanium metal of a quality which, when connected as an anode in
hydrochloric acid, allows the current passage to drop within a
few seconds to practically zero, is covered as an anode core
with a top coat of noble metal and that a blocking film is formed

on the pores by electrolysis of alkali metal chlorides, but in these cases the titanium did not come in contact with nascent chlorine.

Anodes are known which have a core of tantalum or zirconium and a complete or partial coat of platinum. The platinum coat was applied in a thickness of 50 mu, for example. These anodes were developed for electrolytic oxidations, for example, the production of persulfates, hence for electrolyses where the specific action of platinum and platinum metals resp. is required as an anode metal. For electrolyses where oxygen is formed on the anode, the above-mentioned electrodes are highly suitable. But these electrodes could not be used for electrolyses where chlorine is evolved on the anode. In the production of chlorine in continuous operation, the bond between the platinum top coat and the tantalum is not stable, so that platinum particles pass over into the electrolyte after a short time. Anodes, where zirconium is used as a core metal, or alloys consisting mainly of zirconium, also show precipitation after a short time.

Actually, tantalum should be the best suitable metal for the present purpose, since it shows a better corrosion behavior than titanium and forms a protective surface film, when connected as an anode, which is far more resistant and can withstand far higher stresses resp. than titanium. But it was found surprisingly that titanium leads to far better results, particularly because the adhesive strength of a top coat of noble metal on titanium is far better and more stable than on tantalum.

Comparison tests have shown that in a 3% NaC1-solution with cell-voltages between 7-9 volt and a current density of 1500 A/sqm, peelings and blisters with a simultaneous voltage rise appeared on platinum-coated tantlum anodes after a short operating time, which varied between 0.33 and 41 hours, depending on the type of coating, while the corresponding titanium anodes showed no defects after 112 hours, either on the core metal or on the top coat. A corresponding zirconium anode failed after 6 minutes, due to corrosion of the core metal. These results are probably based on the hitherto unknown phenomenon that the corrosion spreads between anode core and top coat in tantalum and other metals, detaching the topcoat, while in titanium the formation of the oxide film remains limited to the areas exposed at the pore openings. Anodes produced on a technical scale according to the invention showed no damages on the core material and on the top coat after a testing time of 1000 hours.

Titanium has already been used for anodes in this form that, starting from a metallic titanium core, a carbon or graphite layer surrounding the latter was impregnated with titanium carbide formed during the melting of the titanium. This was done to avoid the tendency to anodic film formation, characteristic of titanium, and to obtain a firm bond between the graphite and the titanium core. A different procedure was thus used than in the invention, where a very thin coat of noble metal is used to utilize the film formation.

In addition, highly porous, for example, spongy titanium was used for the production of depolarization electrodes as a core material. In these electrodes an outer layer of depolarizing substances, such as manganese dioxide, lead oxide or silver oxide, were applied on the highly porous core. The depolarlization coat can also be produced by treatment with sulfuric acid. In these depolarization electrodes it is also known to coat the titanium core with an intermediate layer of graphite, iron, gold or platinum before the depolarizor material is applied. The basis for the production of these depolarization electrodes is the discovery that highly porous titanium does not form under electrolytic conditions a blocking film hindering the current flow. In contrast, according to the present invention a titanium is used as core material which forms a blocking film under anodic conditions.

Titanium was also used for the production of electrolytic condensers. But in this case too, a blocking film is formed with evolution of oxygen.

It was known that titanium, acting in NaC1-solution as an anode, forms a blocking film as long as oxygen is evolved. But as soon as the formation of chlorine sets in, the blocking film is decomposed and a precipitate of a titanium oxide is formed in the solution. In view of these facts, it could not be foreseen that titanium, covered with a top coat of noble metal, could have a stable blocking film in the electrolysis of media containing chlorine ions.

It is important for the realization of the invention that titanium can form a stable blocking film in aqueous solutions or melts containing chlorine ions, while such a blocking film is only formed in other metals when oxygen is evolved directly on the anode.

For the production of an anode which has, according to the invention, a titanium core coated with a noble metal layer, the blocking film can be formed on the spot, that is, in the elec- trolytic bath in which the coated electrode is to act as an anode. But the blocking film can also be applied by a preceding treatment at the pores on the core metal coated with noble metal.

Preferably the blocking film is applied by a preliminary treatment, namely by electrolysis. It is advisable to form the blocking film at a higher voltage than the voltage in the antici- pated normal use as an anode. This way it is ensured that the blocking film will be stable in operation.

The thickness of the top coats of noble metals used according to the invention can be extremely low, for example, about ½ micron. Preferably the thickness of the top coats is about 1 micron.

The following examples will illustrate the invention.

Example 1.

If titanium is charged into an aqueous solution containing chlorine-ions, for example, hydrochloric acid, and if the titanium is connected as an anode, the current flow drops within a few seconds to practically zero because the titanium is covered with a protective coat which makes the further current flow impossible and protects the underlying material completely.

But if a titanium plate which is coated with a rhodium coat of 1 micron thickness is connected in a hydrochloric acid solution as an anode, the current flow continues unhindered. The pores in the rhodium coat can not damage the underlying titanium, because the latter is protected at the exposed areas by the oxide film formed. This electrode is highly suitable for electrolyses of alkali chloride solutions, because there is practically no wear, the current density can be several times higher than in the know electrodes, and there is no contamination of the electrolyte, so that considerable maintenance costs can be saved.

In addition, a much greater number of these electrodes can be placed into the bath within a certain space, because, compared to graphite or magnetite electrodes, the diameter and space requirement resp. of an electrode according to the invention is much lower.

Since a continuous movement of the bath is of great importance in the electrolysis of alkali metal chlorides, these electrodes can be perforated, if necessary, to obtain a high rate of flow.

Example 2.

An electrode which consists as in Example 1 of titanium with a rhodium top coat of 1 micron thickness, can also be used for the electrolysis of salt melts. To this end, the electrode is connected in an aqueous solution of 20% hydrochloric acid as an anode, while a carbon plate serves as a cathode. The voltage between the two electrodes is gradually increased up to 150 Volt

d-c and is maintained until the titanium plate is covered at
the porous areas of the rhodium coat with a blocking film
through which practically no current can pass.

This electrode is placed in a zinc chloride melt of 330
deg. C. Then the plate is connected as an anode and a carbon
plate is used as a cathode. With sufficient current flow, the
mixture remains at melting temperature even without external
heat supply, while with a reduced current flow heat must be
supplied from the outside. Chlorine is evolved on the anode
and zinc is deposited on the cathode. This way it is possible
to produce high purity zinc.

Naturally this anode can also be used for the electrolysis
of other salt melts. It is of particular advantage that the
melting temperature of titanium is at about 1800 deg.C. and that
of rhodium at 1900 deg.C. It is therefore possible to work at
very high temperatures without any damages. The carbon-graphite
electrodes used for this purpose are far more temperature-sensitive
and are therefore subject to considerable wear.

Claims:

1. Method for the production of an anode for electrolyses of
aqueous or molten electrolytes containing chlorine ions, consisting
of a core of a base metal and of a porous top coat of noble metal,
the core being provided electrolytically with a blocking film at
the areas where the top coat is porous, characterized in that
titanium of such quality is used that, when it is connected in
hydrochloric acid as an anode, the current flow drops within a few

seconds to practically zero, that it is coated as an anode core with a top coat of noble metal, and that a blocking film is formed at the pores by electrolysis in solutions or melts contining chlorine ions.

2. Method according to Claim 1, characterized in that the blocking film is formed at a higher voltage than the voltage in normal use as a anode.

References:

Swiss Patent No. 100,171   -   U.S. Patent No. 2,647,079
Ger. Patent No. 913,768   -   J. of Phys. Chemistry 57 (1953)-p. 262-268

(Translated by Carl Demrick Associates Inc. IE/fs)

[handwritten annotations:]

REF

LINK TO ITEM C ON ~~PARTS LIST~~ ~~ORDOCT~~

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LINKS TO ITEM I ON ~~PARTS LIST~~ ~~ORDOCT~~

(ITEM J)

~~ITEM (ITEM J)~~

HEADINGS *

DISCUSSION *

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EXAMPLES
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CLAIMS
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~~REFERENCES~~ * ➔ P. 9

REFERENCES *!

LINK TO ITEM I
~~ON~~ ~~...~~

TITANIUM   WITH NOBLE-METAL SHEATHS
ELECTRODES ∧ WITH BARRIER LAYERS OF OXIDE AT THE PORES.

CHARGING PROCESSES ON ANODIC POLARIZATION OF TITANIUM

By COLBY D. HALL, JR., AND NORMAN HACKERMAN

Department of Chemistry, The University of Texas, Austin, Texas

Anodic charging curves for titanium in neutral NaCl solutions show a linear potential increase to the oxygen evolution potential. The charge passed is sufficient to deposit three oxygens on each titanium surface atom based on area as determined by measurement of polarization capacity. This corresponds to a monolayer if the oxygen is present as atoms having the same size as covalently bonded oxygen. Potential vs. log time curves for the decay of oxygen overvoltage show that discharge of the double layer capacitance occurs both by a continuation of the oxygen evolution reaction and by flow of current through a resistance. For the latter process, the resistance–capacitance product increases with increasing total time of oxygen evolution. This effect is attributed to the formation of a TiO_2 film. After several hours of continuous oxygen evolution at current densities greater than 10^{-3} amp./cm.^{2}, oxygen evolution ceases and the potential rises to +10 v. These effects are attributed to thickening of the TiO_2 film, which grows by outward migration of titanium ions. The space charge of these excess positive ions in the film can account for most of the measured electrode potential, so that the film-to-solution potential is not sufficient for oxygen evolution. At 10 v., the film breaks down and pitting occurs.

Introduction

The anodic polarization of metals has been studied largely with respect to oxygen overvoltage and the mechanism of oxygen evolution. It is generally accepted that a complete film of oxygen is present on an electrode from which oxygen is being evolved,[1] but there is no general agreement as to whether the film is composed of chemisorbed oxygen or of metal oxide. It is recognized, of course, that the mechanism may not be the same for all metals and for all experimental conditions.

Bowden[2] measured the charge required to change a platinum electrode from the reversible hydrogen potential to the reversible oxygen potential, and *vice versa*. The potential–time curves showed arrests whose length depended on the duration of previous hydrogen or oxygen evolution. Except for the charge passed during the arrests, a definite quantity of 3×10^{-3} coulomb/cm.^{2} was required for the change. The arrests during cathodic polarization were considered to represent removal of an oxide of platinum. The potentials of the arrests were the same as those measured for a PtO_2-coated platinum wire in the corresponding solutions.

Armstrong, Himsworth and Butler[3] do not agree that an oxide is formed on platinum during oxygen evolution. They attribute the arrest to a high local concentration of oxygen, since they found the potential to be affected considerably by stirring. They say, however, that an oxide is formed on gold.

Pearson and Butler[4] found that the potential-time curve for the anodic polarization of platinum from the hydrogen evolution potential to the oxygen evolution potential contains two linear regions, for which the charges passed are sufficient to remove a monolayer of hydrogen atoms and to deposit a monolayer of oxygen atoms.

Hickling and co-workers[5] studied the anodic behavior of Pt, Au, Ni, Ag, Cu and Co by an oscillographic method, and observed potential–time curves having linear portions. Hickling attributes rapid increases of potential to charging of a double layer, and the slower linear increases to formation of films of metal oxides of definite composition. He found that changes of slope occur at the reversible potentials of metal/oxide or lower oxide/higher oxide electrodes. El Wakkad and Emara,[6] using Hickling's method and also a direct method found evidence for the consecutive formation of PtO and PtO_2.

Titanium offers an example of a metal quite active in the e.m.f. series which, nevertheless, exhibits a marked degree of passivity toward dissolution and toward anodic dissolution. The present authors have measured the cathodic and anodic polarization of titanium.[7] Further investigations have now provided additional information on the processes involved in the anodic polarization of titanium.

Experimental Procedure

Apparatus.—Polarization measurements were made by the direct method, in a circular path apparatus, using saturated calomel half-cells as the reference electrodes. The titanium coupons were polished on No. 2/0 metallographic paper and cleaned by rubbing with filter paper moistened with ethyl alcohol, then with dry lens tissue. For most of the measurements, the coupons were 5.0 cm.^{2} in projected area and were cast in a plastic wafer which was inserted into a machined plastic holder so that the coupon was flush with the face of the holder. These are designated as "flush coupons." One series of measurements was made with a coupon of 4.0 cm.^{2} projected area, mounted in a machined plastic holder in such a way that the exposed face of the coupon was recessed $^3/_{32}$ inch behind the face of the holder. This is designated as a "recessed coupon." Further details of the apparatus are described elsewhere.[7]

Materials.—The titanium was made by the Remington Arms Company. Spectrographic analysis showed that it contained over 99% Ti, with 0.725% C, 0.25% Fe, and traces of other elements. All measurements were made in 0.50 M NaCl solution, made up from analytical reagent grade NaCl and distilled water. The solutions were kept saturated with air and were held at 30°.

Surface Area.—The surface area of the titanium coupons was determined by a capacitance method based on that of Wagner.[8] The roughness factor, or ratio of real to projected area, was found to be 10 ± 3. A measurement of surface area by krypton adsorption, obtained quite recently, gives the roughness factor as 2.2 ± 0.2. It is not entirely clear at this time which of these values is correct. The interpretation of the results has been made on the basis of the earlier measurement.

(1) N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., p. 326.

(2) F. P. Bowden, *Proc. Roy. Soc.* (London), A125, 446 (1929).

(3) G. Armstrong, F. R. Himsworth and J. A. V. Butler, *ibid.*, A143, 89 (1933).

(4) J. D. Pearson and J. A. V. Butler, *Trans. Faraday Soc.*, 34, 1163 (1938).

(5) A. Hickling, *ibid.*, 41, 333 (1945); *ibid.*, 42, 518 (1946); A. Hickling and J. E. Spice, *ibid.*, 43, 762 (1947); A. Hickling and D. Taylor, *Discussions Faraday Soc.*, 1, 277 (1947); *Trans. Faraday Soc.*, 44, 262 (1948); S. E. S. El Wakkad and A. Hickling, *ibid.*, 46, 820 (1950).

(6) S. E. S. El Wakkad and S. H. Emara, *J. Chem. Soc.*, 461 (1952).

(7) C. D. Hall, Jr., and N. Hackerman, to be published.

(8) C. Wagner, *J. Electrochem. Soc.*, 97, 71 (1950).

Quantities which involve area are given in terms of *projected* area unless designated otherwise. Where *real* area, based on a roughness factor of 10, is meant, the abbreviation cm.^{2}$_{real}$ is used.

Results

All potentials are given on the saturated calomel electrode scale and are good to 0.01 v. in all cases unless otherwise noted.

Anodic Charging Curves.—Charging curves for the anodic polarization of titanium at constant current densities are shown in Fig. 1. Curve 1 is a potential-time curve for a coupon which was left on open circuit. Curve 2 is referred to both the time and the charge density scales. Except at the lowest current density, the charge required to reach a constant oxygen evolution potential is approximately the same at all current densities shown. The average is 1.45×10^{-2} coulomb/cm.^{2}. The potential increase is linear for current densities of 2×10^{-7} amp./cm.^{2} and larger, and the rates of increase are about equal, as may be seen in curves 4 through 7. At the smaller current densities of curves 2 and 3, the initial rate of increase is greater than that of the later portions of the curves.

Polarization at Higher Current Densities.—Figure 2 shows potential-time curves for flush coupons polarized at 2×10^{-3} amp./cm.^{2} and at 6×10^{-3} amp./cm.^{2}, and for a recessed coupon polarized at 6×10^{-3} amp./cm.^{2}. At these current densities, the initial linear rise of potential is too rapid to show up on the figure. After reaching the oxygen evolution value, the potential remains constant for one to several hours, then begins a constantly accelerating increase which continues to +9 to +10.5 v. It then fluctuates erratically over a range of ±0.4 v., but maintains a fairly constant average value. At the beginning of the rapid potential rise, visible evolution of oxygen ceases. Shortly thereafter, the surface of the titanium develops a thin, transparent brown film. At +10 v., this film changes to a dark blue, and pits develop on the coupon surface. As the pits grow, a white, gelatinous precipitate of hydrous titanium oxide is formed in the solution.

Anodic Polarization Decay and Repolarization.—A coupon which had reached a constant potential of +0.19 v. on open circuit was then polarized anodically at 2×10^{-7} amp./cm.^{2}. The potential increased rapidly to +0.55 v., where it remained constant for about 40 minutes, then increased linearly with time at a rate equal to that of a freshly prepared coupon polarized at the same current density, and finally became constant at the oxygen evolution potential, +0.97 v. Another coupon which had been polarized cathodically at $2 + 10^{-8}$ amp./cm.^{2} to a constant potential of +0.12 v. was made anodic at the same current density. The potential increased fairly rapidly to +0.25 v., remained constant for about 3 hours, and then increased again at a rate about equal to that of a fresh coupon at the same current density.

These effects were further investigated in a series of measurements in which a coupon was alternately polarized anodically and left on open circuit. The sequence of steps of polarization and decay of polarization may be followed in the potential-time curve of Fig. 3. The current was started at the times designated by odd-numbered points, and was
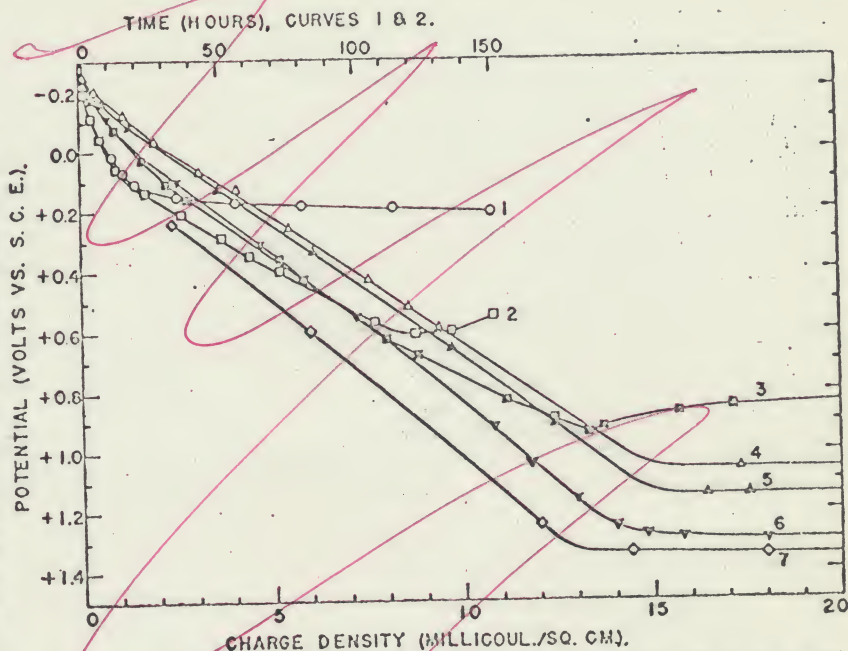

Fig. 1.—Anodic charging curves for titanium in aerated 0.5 *M* NaCl at 30°: 1, 0.0 amp./cm.^{2}; 2, 2.0×10^{-8} amp./cm.^{2}; 3, 6.0×10^{-8} amp./cm.^{2}; 4, 2.0×10^{-7} amp./cm.^{2}; 5, 6.0×10^{-7} amp./cm.^{2}; 6, 6.0×10^{-6} amp./cm.^{2}; 7, 2.0×10^{-5} amp./cm.^{2}.
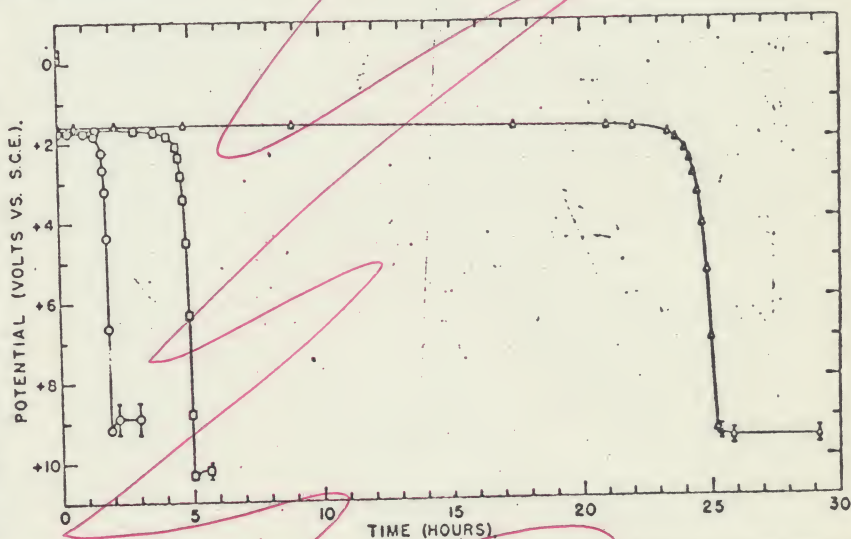

Fig. 2.—Time-potential curves for anodic polarization of titanium in aerated 0.5 *M* NaCl at 30°: Δ, 2.0×10^{-3} amp./cm.^{2}, flush coupon; ○, 6.0×10^{-3} amp./cm.^{2}, flush coupon; □, 6.0×10^{-3} amp./cm.^{2}, recessed coupon.

stopped at times designated by even-numbered points. The potential-time curves for polarization and for polarization decay are shown on a larger scale in Figs. 4 and 5, respectively, in which the time scales start at the instant of starting or stopping the current. These curves are numbered to correspond to the sections of Fig. 3 beginning with the indicated number, e.g., curve 2 extends from point 2 to point 3. Figure 6 shows the data for polarization decay, plotted as potential *vs.* log time.

The anodic current density was 6×10^{-6} amp./cm.^{2} in the original polarization of curve 1, and in the repolarizations of curves 3, 5, 7 and 9. In the repolarizations of curves 11 and 15, the current density was 2×10^{-7} amp./cm.^{2}. At point 13, *cathodic* polarization was started at 2×10^{-7} amp./cm.^{2}, and the current density was increased in steps to 2×10^{-4} amp./cm.^{2}, where it was held for 45 minutes. At this current density, hydrogen was evolved slowly at a potential of −1.20 v. After the cathodic current was stopped, the potential increased, finally becoming constant as shown in the last part of curve 14, Fig. 3.
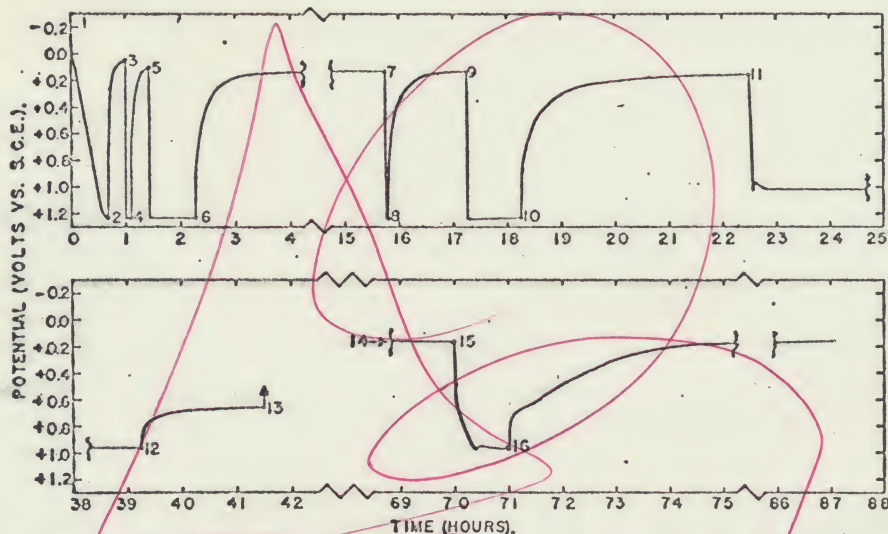
Fig. 3.—Time-potential curves for anodic polarization, depolarization and repolarization of titanium in aerated 0.5 M NaCl at 30°. The odd numbers indicate time at which current was started and the even numbered points show times at which current stopped.

The rate of increase of potential for the original polarization, curve 1 of Fig. 4, is the same as that for the polarization at the same current density shown in curve 6 of Fig. 1. In each subsequent repolarization at 6×10^{-6} amp./cm.^{2}, the potential reached the oxygen evolution potential, $+1.23$ v., in less than the 30 seconds required to make the first reading. By repolarizing at 2×10^{-7} amp./cm.^{2}, it was possible to follow the potential increase as shown in curves 11 and 15. From curve 11, it is calculated that the capacitance of the titanium surface is 3 μfd./cm.^{2}real, and the charge required to repolarize to the oxygen evolution potential is 4×10^{-4} coulomb/cm.^{2}real.

Discussion

Anodic Charging Process.—The increase of potential in the original polarization of a freshly prepared titanium coupon is proportional to the quantity of electricity that has passed, and therefore presumably to the amount of oxygen that has been deposited on the surface. However, the measurements on polarization decay and repolarization show quite clearly that the phenomenon is more complex, and that the potential is not, under all conditions, simply a function of the quantity of oxygen present on the surface. The results indicate that two distinct processes occur simultaneously: anodic deposition of oxygen on the titanium surface, and charging of an electrical double layer.

The original polarization to the oxygen evolution potential requires a charge 360 times as great as that required for repolarization after the polarization has been allowed to decay on open circuit. It is obvious that the original polarization produces a change on the surface which is not reversed by standing on open circuit. This irreversible change may be best explained as the deposition of a layer of chemisorbed oxygen. The charge used in depositing oxygen is essentially equal to the total charge of the original polarization. It is equal to 9.0×10^{15} electrons/cm.^{2}. The area occupied by each atom in the titanium surface may be calculated to be 7.4×10^{-16} cm.^{2}. Thus, the polarizing charge is equivalent to 6.6 electrons for each titanium atom in the surface, and can deposit, on the

area occupied by each titanium atom, about 3.3 atoms or ions of oxygen.

It is not possible to determine with certainty whether the oxygen in the chemisorbed layer is present as O$^-$ ions, or whether the ions have given up their electrons to the metal and remain as O atoms. However, this question may be considered from the standpoint of the sizes of the two types of particles. The radius of an oxide ion in ionic crystals is 1.40×10^{-8} cm. Taking this as an approximation of the radius of a chemisorbed oxide ion, the area occupied by each ion in a hexagonally close-packed layer is 6.8×10^{-16} cm.^{2}, and there are 1.5×10^{15} O$^-$/cm.^{2} in a monolayer. The charge passed in polarizing to the oxygen evolution potential is equivalent to 4.5×10^{15} O$^-$/cm.^{2}real, or three layers of oxide ions. It does not seem likely that the electrostatic repulsion of these closely packed negative particles would permit a film three layers deep to have the degree of stability observed for the chemisorbed oxygen. In the strong electric field present at the oxygen evolution potential, dipole attraction between the highly polarizable oxide ions would assist in stabilizing the film, but this effect would largely disappear on open circuit, and repolarization would then require a larger charge than is observed.

The radius of covalently bonded oxygen, 0.74×10^{-8} cm., may be used as an approximation of the radius of a chemisorbed neutral oxygen atom. The area for each atom in a hexagonally closed-packed layer is then 1.9×10^{-16} cm.^{2}, and there are 5.3×10^{15} O/cm.^{2} in a monolayer. The original polarizing charge can thus deposit 4.5/5.3, or 85%, of a monolayer. The difference between this and a complete monolayer may be accounted for either by the uncertainty in the value for the roughness factor, or by assuming that some hydroxyl radicals are included in the layer. This approximation of a monolayer and the lack of repulsion between the neutral particles, provide good arguments for assuming that the chemisorbed oxygen is present as neutral atoms.

The increase of potential with time at zero applied current density is obviously caused by some process which occurs spontaneously on the titanium surface. This process is assumed to be the chemisorption of oxygen from the aerated solution. According to the electron configuration theory of passivity,[9] such a chemisorbed film causes the potential of the metal to become more noble by satisfying the residual valence forces of the metal atoms in the surface. Uhlig[10] considers this "chemical passivity" to be "the important factor in explaining

(9) H. H. Uhlig and J. Wulff, Trans. Am. Inst. Mining Met. Engrs., 135, 494 (1939); H. H. Uhlig, Trans. Electrochem. Soc., 85, 307 (1944).
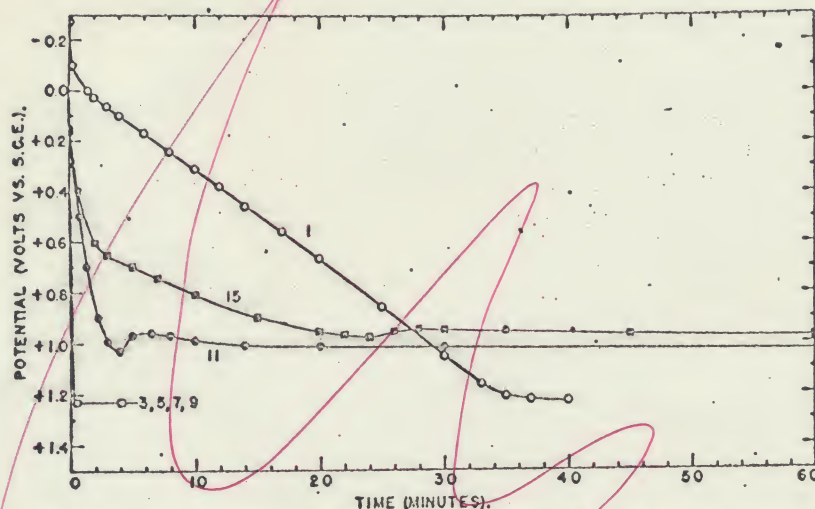(10) H. H. Uhlig, J. Electrochem. Soc., 97, 215C (1950).

Fig. 4.—Time–potential curves for anodic polarization and repolarization of titanium in aerated 0.5 M NaCl at 30°. (For explanation of curve numbers, see Fig. 3.) ○, 6×10^{-6} amp./cm.²; ⊙, 2×10^{-7} amp./cm.²

since a part of the oxygen in the adsorbed layer originates as O_2, and does not require current for its adsorption.

Decay of Anodic Polarization.— When the current to an anode is stopped during oxygen evolution, the reaction must continue at a rate determined by the potential. The double layer is discharged, and the potential decreases. Armstrong and Butler[11] show that, for an electrode reaction whose rate is $I = ke^{aE}$, the potential during decay of overvoltage follows the equation $E = K - 0.12 \log t$, where K is a constant and t is time after stopping of the current. The present results for titanium show partial agreement with this equation, as may be seen in Fig. 6. Curves 6, 8 and 10 have short arrests of slope about -0.12 in the region of $+0.8$ v. Curve 12 and curve 16 down to $+0.65$ v., are almost linear, and have slopes of -0.10 and -0.12, respectively. At lower potentials, all of the curves except curve 12 have slopes of about -0.5, until they level off at $+0.05$ to $+0.16$ v. The length of the arrest having a slope of -0.12 is

corrosion resistance of metals . . . such as . . . titanium . . .'' The process of spontaneous passivation approaches its limit as the potential approaches $+0.2$ v. This potential, attained by a fresh coupon when left on open circuit is approximately the same as that attained in the decay of the oxygen overvoltage. It apparently represents the zero-current potential of titanium on which oxygen is chemisorbed, either spontaneously or by anodic deposition.

The adsorption of oxygen, increasing the potential in proportion to the number of atoms adsorbed, can account for only a part of the potential increase during the original polarization, since the potential after open-circuit decay of polarization is only $+0.2$ v., even though all of the adsorbed oxygen is known to be still present. The major portion of the increase to the oxygen evolution potential must occur in the diffuse double layer. The capacitance of this double layer, as determined from the initial rate of increase of potential in repolarization, is about 3 μfd./cm.²$_{real}$. This is smaller than the capacitance usually measured on an anode or cathode surface.

At very low applied current densities, the charging curves (Fig. 1) are non-linear in their early portions. This is because the initial rate of chemisorption of dissolved oxygen is greater than the rate of deposition of oxygen from OH^- by the applied current. At potentials higher than $+0.2$ v., the spontaneous chemisorption does not occur, and the potential increase is then linear at the rate determined by the applied current density. The total charge passed by the applied current in reaching a constant potential is less than at higher current densities,

greater with longer time of previous oxygen evolution. Comparison of curves 6 and 8 shows that the arrest is shortened slightly by prolonged standing on open circuit during the step of curve 6. The arrest is shortened also by cathodic treatment preceding an anodic polarization and polarization decay, as shown by curves 12 and 16.

If a capacitance C is charged to a potential E'_0, and discharged through a resistance R, the potential E' during discharge is $E' = E'_0 e^{-t'/RC}$, where t' is in seconds, R is in ohms, and C is in farads. This
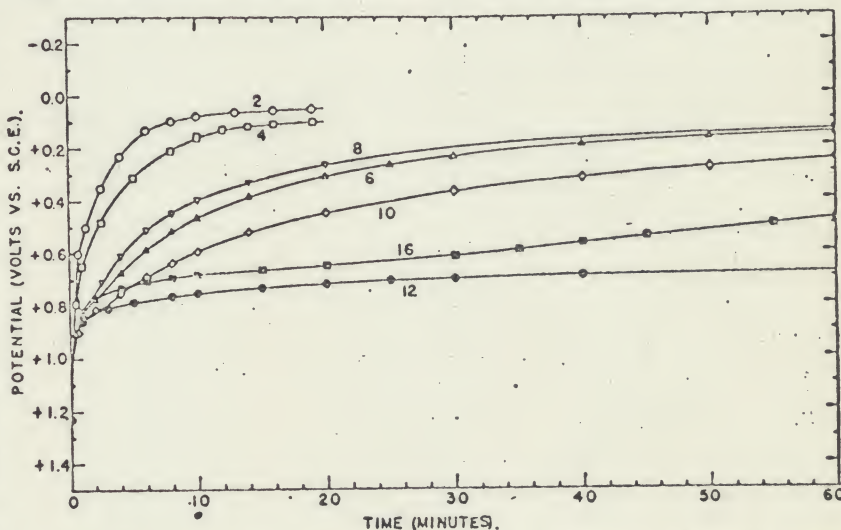

Fig. 5.—Time–potential curves for open-circuit depolarization of titanium, following anodic polarization, in aerated 0.5 M NaCl at 30°. (For explanation of curve numbers, see Fig. 3.) ○, following 6×10^{-6} amp./cm.²; ⊙, following 2×10^{-7} amp./cm.²

(11) G. Armstrong and J. A. V. Butler, *Trans. Faraday Soc.*, **29**, 1261 (1933).

function may be written

$$t' = -2.3RC \log E'/E_0', \text{ or}$$

$$\log t' = 0.36 + \log RC + \log (-\log E'/E_0')$$

A plot of E' vs. $\log t'$ is a sigmoid curve asymptotic to $E' = E_0'$ and to $E' = 0$. Its middle portion is nearly linear. The maximum slope, which occurs at $E' = E_0'/e = 0.37 E_0'$, is

$$dE'/d \log t' = -2.3E_0'/e = -0.85E_0'$$

The slope thus depends only on E_0'. A change in RC shifts the entire curve along the $\log t'$ axis. A family of such curves having different values of RC strongly resembles the curves of Fig. 6 at potentials below the arrest. This suggests that the potential below the arrest is controlled by the discharge of the double-layer capacitance through a leakage resistance, and that the effect of increasing the time of oxygen evolution is to increase the value of the product RC.
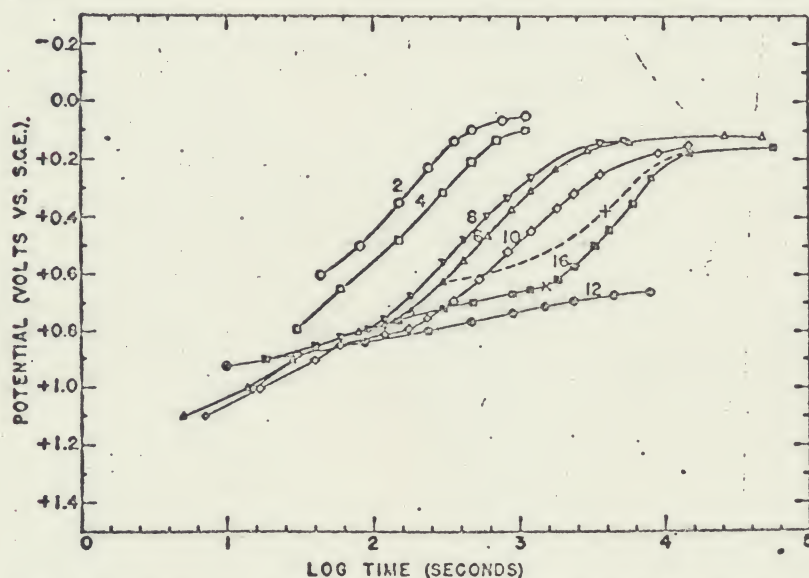

Fig. 6.—Potential vs. log time for open-circuit depolarization of titanium, following anodic polarization, in aerated 0.5 M NaCl at 30°: O, following 6 × 10^{-4} amp./cm.^{2}; $\oslash$, following 2 × 10^{-7} amp./cm.^{2}.

Since the length of the arrest in Fig. 6 depends on the total time of previous oxygen evolution, rather than on the duration of the immediately preceding polarization step, it is obvious that whatever causes the lengthening of the arrest is not substantially lost during polarization decay. It is known that a visible TiO$_2$ film is formed on the surface after oxygen evolution ceases at high current densities, and it is likely that some TiO$_2$ forms during oxygen evolution. It is, therefore, probable that TiO$_2$ also forms, although very slowly, at low current densities. The gradual accumulation of TiO$_2$ could quite conceivably cause an increase of RC, and thereby lengthen the arrest. Cathodic polarization would be expected to remove some TiO$_2$ and shorten the arrest.

All of the curves of Fig. 6 are in accord with an assumption that the double layer is discharged by two processes, one a logarithmic function, the other an exponential function of time. The first process is oxygen evolution, which requires the passage of electrons through the double layer

boundary at the metal surface. The second process is leakage of current around the double layer boundary through an external resistance. The two discharge paths are electrically in parallel, so that the currents are additive. In the early part of each discharge, the oxygen evolution current is the larger, and the potential follows the logarithmic equation, giving a linear E vs. $\log t$ plot. As E approaches the reversible oxygen potential, the current for oxygen evolution approaches zero. When it becomes smaller than the leakage current, the potential obeys the exponential decay law, giving a sigmoid E vs. $\log t$ curve. In successive steps of polarization decay, following longer oxygen evolution, the amount of TiO$_2$ on the surface becomes larger. Thus RC is larger and the leakage current is smaller. The arrest, i.e., the logarithmic decay, is lengthened, since it continues so long as the oxygen evolution current is larger than the leakage current. In curves 2 and 4, the arrest apparently ended before the first reading was made.

The sigmoid portions of the experimental curves do not have exactly the same shape and slope as the theoretical E' vs. $\log t'$ curves, because the time scale is not based on the start of the exponential decay. Since the exponential equation applies only after the oxygen evolution current becomes negligible, the proper initial values, i.e., $E' = E_0'$ at $t' = 0$, are those existing at the time of changeover of control from logarithmic to exponential. Since the currents for the two types of discharge are comparable near the changeover, it is not very sharp, but it may be taken to be the end of the linear arrest. If the potential and time at this point are designated as E_c and t_c, and the final constant potential as E_f, then $E_0' = E_c - E_f$, and $t' = t - t_c$. In Fig. 6, the apparent changeover point on curve 16 is marked with an X, at $t_c = 1500$ seconds, and E vs. $\log t'$ is plotted as a broken line. Similar curves for the earlier polarization decay steps would lie closer to the $\log t$ curves. A value for E_0' may be obtained from each curve as $-(dE/d \log t')_{max}/0.85$.

These values probably are more reliable than those calculated as $E_c - E_f$, because of the indefiniteness of the changeover point. The exponential decay equation shows that when $t' = RC$, $E' = E_0' e^{-1} = 0.37E_0'$. Thus, RC may be obtained from the experimental curves at t' when $E = E_f + 0.37 E_0'$. For curve 16, this point is marked with a + in the broken curve. The values of RC are: curve 2, 210 sec.; curve 4, 310 sec.; curve 6, 1200 sec.; curve 8, 930 sec.; curve 10, 2400 sec.; and curve 16, 4000 sec. From curves 2 and 10 it is seen that RC increases more than 10 times in 2 hours of oxygen evolution.

Anodic Processes at High Current Densities.— The TiO$_2$ film which forms on the metal surface during oxygen evolution is considered to be dis-

tinct from the layer of chemisorbed oxygen which is deposited during the linear potential rise in the original polarization. The basis for the distinction is that the titanium atoms on which oxygen is chemisorbed are not removed from the metal lattice, whereas this removal is required for the formation of the metal oxide. It is probable that titanium atoms are removed from the metal lattice only at the rather high positive potential which exists on the electrode during oxygen evolution. The higher oxygen overvoltage at larger current densities thus accelerates the formation of TiO_2. However, even at high current densities only a small fraction of the total current is used in forming TiO_2 during oxygen evolution. This is shown not only by the active evolution of oxygen bubbles, but also by the lack of a visible oxide film until after oxygen evolution has stopped.

The appearance of a visible surface film shortly after the cessation of oxygen evolution suggests that the cessation is caused by some degree of completion of a TiO_2 film. It is not likely that just a uniform monolayer is formed, since this would require that TiO_2 be formed more easily where the metal is covered by chemisorbed oxygen than where some oxide is already present. According to Uhlig's theory of passivity, the adsorption of oxygen on a metal atom decreases the tendency for that atom to react, whereas the removal of the atom from the metal lattice to form an oxide molecule exposes the underlying atoms and permits it to react. Thus there should be a preference for further reaction where some oxide is already present. After a spot becomes several layers thick, further thickening requires a higher potential, and there is then an increasing tendency for spreading of the spot by formation of TiO_2 at the edges. Thus the spots of oxide film can grow both by thickening and by spreading laterally over the surface.

It is seen in Fig. 2 that there is no sharp break in the curves at the beginning of the second potential rise. The cessation of oxygen evolution, which occurs at about +2 v., may be taken as the dividing point between the constant or slowly rising potential and the rapid potential increase. For reasons presented later, it is presumed that oxygen evolution is diminished where an oxide film is present, and is prevented where the film is sufficiently thick. Thus, as the area of the uncoated surface decreases, the current density for oxygen evolution, and the oxygen overvoltage, must increase. This can account for the slow increase of potential during oxygen evolution which is seen in Fig. 2. As the area of the uncoated surface becomes smaller, a given increase in the coated area constitutes a larger percentage decrease in the uncoated area. Also, as the potential becomes higher, the rate of formation of TiO_2 increases, until, just before the film is completed, this process uses almost all of the applied current. Both of these effects tend to cause the acceleration in the potential increase which occurs shortly before oxygen evolution stops.

After the cessation of oxygen evolution, all of the current is available to form TiO_2, and the film thickens rapidly. The formation of TiO_2 requires the movement of either titanium or oxide ions through

the TiO_2 film. The positive titanium ions are much smaller than the oxide ions, and, therefore, are almost certainly the ones involved in the migration. They leave the surface as a result of the applied potential, pass through interstitial positions in the TiO_2 film, and combine with oxide ions at the film-solution interface.

In a recent paper,[12] Haring has proposed a mechanism for the formation of an oxide film on a tantalum anode, and for the rectifying properties exhibited by this film. Although there are marked differences between the behavior of tantalum and that of titanium, Haring's mechanism for film growth and film breakdown seem to apply to the behavior of titanium during the second anodic potential rise. Haring proposes that the positive metal ions in transit through the oxide film constitute a space charge which is balanced by oxide ions adsorbed on the outer surface of the film. The concentration of excess positive ions is greatest near the metal surface and falls off toward the solution. This unsymmetrical charge distribution constitutes a potential gradient which is maintained by the applied potential. A certain minimum potential gradient is required for movement of the metal ions through the oxide. An applied potential gradient in excess of the minimum accelerates the removal of metal ions from the metal surface and their migration through the oxide film, so that the actual potential gradient during film growth is maintained at a value only a little above the minimum. The total potential difference through the film thus is proportional to the thickness of the film. The measured potential of the electrode consists of this potential difference plus the potentials across the metal/oxide and the oxide/solution interfaces. The oxide/solution potential is the only part of the total potential which is available for the oxidation of OH^- to O_2, and during film growth, prior to film breakdown, this potential is not large enough to cause oxygen evolution. This can explain the lack of oxygen evolution on titanium during the second potential rise. The same considerations apply to the oxide-coated spots during oxygen evolution. At these sites, most of the electrode potential lies within the field of the space charge in the oxide, while on the uncoated areas the full potential is available to produce oxygen evolution.

Haring's mechanism for film growth requires an approximately linear increase of potential at constant current, at a rate proportional to current density. Figure 2 shows that the rate of increase on titanium increases with time and is not proportional to current density. The discrepancy probably is caused by the necessity for completing the coverage of the surface and by film defects where impurities are present in the metal surface. Also, non-uniform current distribution on the coupon surface may play a part. This effect shows up in the different behavior of the flush-mounted and the recessed coupons at the same current density. The sharp edge of the flush coupon was not in close contact with the plastic mounting and so was exposed to the solution. There was thus a concentration of current at and near this edge. The re-

(12) H. E. Haring, *J. Electrochem. Soc.*, 99, 30 (1952).

cessed coupon was bounded by a plastic gasket pressed against its face, so that only a plane surface was exposed, giving a more uniform current distribution.

According to Haring, the total charge carried by the excess positive ions within the film increases as the oxide film thickens. This requires a corresponding increase in the number of oxide ions adsorbed on the outer surface of the oxide film, and causes an increase in the potential across the oxide/solution interface. When this latter potential becomes large enough, oxygen evolution begins again. This reaction, unlike the reaction of metal ions with oxide ions involved in film growth, yields electrons at the solution side of the film. These electrons, in moving through the film toward the metal, neutralize some of the positive metal ions, thereby decreasing the space charge and permitting the movement of more positive ions from the metal into the film. These ions tend to follow the path of best conductance established by the inward-moving electrons. The result is a sporadic pattern of film growth and local breakdown of the film.

The local film breakdown would be expected to occur at the areas of highest current density, i.e., at the edges of the flush coupons. This is where pits were found after the potential had been at +10 v. for a while. Film breakdown at points along the sharp edge would cause further concentration of the current at these points. In these pits, titanium ions are removed from the metal so rapidly that they move some distance away from the surface before combining with oxide or hydroxyl ions, so that a hydrous oxide precipitate forms, instead of an adherent oxide film. It should be noted that while the pits are enlarging, the growth of the compact film continues on the rest of the surface, at a potential of about 10 v. This very high potential at the pits probably cannot be attributed to a potential through a remaining oxide film, but instead is probably caused by large ohmic resistance and concentration polarization effects in the electrolyte within the pits, where the current density is very high.

There is no experimental evidence that oxygen evolution begins on titanium at the end of the second potential rise, i.e., at 10 v. Some bubbles were observed at the edges of the coupons, but these could be due to the aeration of the solution, or to the earlier oxygen evolution. However, the evolution of a visible quantity of oxygen probably would not be required to initiate film breakdown by Haring's mechanism. After breakdown has occurred at a few points, the electrode reaction at these points may change to the direct anodic oxidation of titanium, followed by precipitation of the ions as a hydrous oxide.

THE EFFECT OF ULTRASONIC WAVES ON HYDROGEN OVERVOLTAGE[1,2]

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The effects of ultrasonic waves on hydrogen overvoltage have been investigated at 300 kc./sec. in terms of a bright platinum surface. Polarization measurements have been made by the indirect method with an electronic commutator and gated potentiometer. The acoustical amplitude has been determined with a calibrated barium titanate hydrophone. In the absence of ultrasonic waves, the overvoltage has been found to follow the Tafel equation in both sulfuric and hydrochloric acid solutions at current densities from 0.2 to 30 ma./cm.² with a Tafel slope of 0.03 and an intercept constant of 0.12. The decay of the overvoltage with time has been observed to be as low as 1 mv. during a period of 0.001 sec. following the interruption of the polarizing current. These results support the theory that the atomic combination step is responsible for hydrogen overvoltage on platinum. The Tafel slope has been found to depend to a minor extent on the type and the concentration of electrolyte. Ultrasonic waves at cavitation levels produce a decrease in the overvoltage without modifying the Tafel slope. Approximately two-thirds of this depolarization persists after the radiations have ceased. The initial values for the polarization before irradiation are recovered if the polarizing current is turned off for a matter of minutes. The instantaneous component of the depolarization is explained on the basis that the ultrasonic waves greatly reduce the concentration gradient with respect to dissolved molecular hydrogen at the electrode surface. The residual depolarization is interpreted in terms of the stripping off of irreversibly adsorbed species on the surface. The latter probably are adsorbed at the lower potential of the electrode prior to passage of polarizing current and are not readily readsorbed at the more cathodic potential of the polarized electrode.

Introduction

Ultrasonic waves are capable of producing a.c. as well as d.c. changes in the potential of a polarized gas electrode such as the hydrogen electrode. The former effect[3] appears to depend primarily on the modulation of the IR drop in the immediate vicinity of the electrode as a result of the periodic variations produced in the bubble size by the ultrasonic waves. The d.c. effect is more interesting in terms of fundamental information concerning polarization. Ultrasonic waves would be expected to produce a decrease in the polarization associated with a hydrogen electrode for the following two reasons.

(3) E.g., E. Yeager and F. Hovorka, J. Electrochem. Soc., 93, 14 (1951); E. Yeager, J. Bugosh, H. Dietrick and F. Hovorka, J. Acoust. Soc. Am., 22, 686 (1950).

(ITEM I)

HEADINGS *
SUMMARY *
TEXT NOT INPUT

Hall and Hackerman have written
~~this is~~ an article on the mechanisms of film formation
on electrodes.

                    and spread
The nature ∧ of the oxide film on titanium is not
well understood. It is hypothesized by some to be
chemically ~~Oxid~~ absorbed oxygen, * by others to be a true oxide layer.
Hall and Hackerman believe ~~these~~ are both present, but the spread of the
∧ affects the former. * The irregularities in the speed of ~~electrode~~ ~~oxide film formation~~
have to do with the sequence of surface changes: *

ITEM G

No. 661,462

ISSUED   Apr. 16, 1963
CLASS   204-155

ITEM.G

CANADIAN PATENT

METHOD OF MANUFACTURING AN ELECTRODE COMPOSED OF A CORE OF TITANIUM AND A POROUS COATING OF A NOBLE METAL

Henri B. Beer, The Hague, Netherlands

Granted to Amalgamated Curaçao Patents Company N. V., Willemstad, Curaçao, Netherlands Antilles

INVENTOR: HENRI B. BEER
TITLE:

DATE OF FILING: 5 FEB 1960
COMPANY: AMALGAMATED CURACAO
PATENTS CO. N.V.

CANADIAN PATENT. 661,462
(ITEM G)

APPLICATION No.   792,018
FILED   Feb. 5, 1960
PRIORITY DATE   Feb. 6, 1959 Netherlands

No. OF CLAIMS   14 - No drawing

79

In Canadian patent 604,415, issued August 30, 1960, there is disclosed an anode composed of a core of titanium and a porous coating of a noble material or another electricity conducting resistant material, the core of which is electrolytically provided with a barrier layer of titanium oxide in the places where the coating is porous. According to said application the barrier layer is provided after the core has been provided with the coating.

According to Canadian Patent No. 623,718, issued
July 11, 1961, the barrier layer is likewise provided after
the core has been provided with a porous coating of a
noble metal or another electricity conducting material, but

5   according to said patent, the formation of the barrier layer
is effected by a chemical and/or a thermal treatment whereby
the barrier layer is obtained in a stable form which is
substantially chemically inert. According to said patent,
it is possible, for example, to convert the extremely thin

10 layer of oxide already present on commercial titanium into
another stable form of titanium oxide by heating the
titanium in contact with the air.

The present invention is based on the insight that
in the manufacture of an electrode of the above type
mentioned herein, namely an electrode consisting of a core

15 of titanium and a porous coating of a noble metal, it is
of advantage to cause the barrier layer of titanium oxide
to form before the coating is applied.

I have found namely that of all of the so-called
filmforming metals only titanium has the particular

20 property that if it is entirely covered with a layer of
the oxide and is afterward provided with a coating of a
noble metal, it does not at all interfere with the
electronic current-passage therethrough.

The filmforming metals i.e. the metals which have their surface easily oxidized by contact with the air generally appear owing to the presence of an oxidefilm to offer a great resistance against the passage of current both against the ionic currentpassage - e.g. as electrode in an electrolysis bath and against the electronic currentpassage - e.g. in the case of a metal-metal contact. Thus an electrode having a core of aluminium, which metal has been oxidized in the air or has intentionally been provided with a layer of oxide (e.g. by anodising it) and a coating of a noble metal offers a great resistance against the passage of electric current.

The invention, therefore, relates to a method of manufacturing an electrode composed of a core of titanium and a coating of a noble metal, which method is characterized in that the core of titanium prior to being provided with the coating, is electrolytically or thermally and/or chemically provided with a layer of titanium oxide.

In carrying out the method according to
the invention it is not necessary and even entirely
superfluous to free the surface of the titanium
from the adhering oxide film by pickling, e.g. in
5   a solution containing hydrogen fluoride and to
coat the pickled surface as soon as possible in
order to prevent that a fresh layer of oxide
will form upon contact of said surface with the
air.

10   Seeing that it is the intention to provide
the titanium whereever it will come into contact
with the electrolyte, with a barrier layer of
titanium oxide said barrier layer may be provided
without removing the oxide film naturally present
15   by pickling. The application of the barrier layer
may be effected both electrolytically and by a
chemical and/or a thermal treatment. In the
electrolytic method it is advisable to form the
barrier layer at a voltage higher than the
20   voltage which will be normally applied when the
electrode is used as anode. The chemical and/or
thermal treatment is preferably effected by
heating the metal in an oxidizing atmosphere at
a temperature up to about 700°C. In a neutral or
25   even a weakly reducing atmosphere it will also
be possible to heat the metal at a slightly higher
temperature. In both cases best results are
obtained by gradually cooling the titanium thus
treated.

When applying the coating of a noble metal
care should be taken that the reducing conditions
required therefor are not of such a nature that the
barrier layer of titanium oxide formed is adversely
affected. When the coating is galvanically deposited
the electrolysis should take place at a low voltage
so that not too much hydrogen is liberated at the
cathode. Also in the case of a chemical or semi-
electrolytical deposition of the noble metal - e.g.
by reduction of salts of noble metals or by the so-
called "brushing method" - the necessary precautions
should be taken to prevent an injurious reduction of
the barrier layer of titanium oxide. This will be
further elucidated in the examples.

An advantage of the electrode manufacture by
means of the method according to the invention is that
it is certain now that in all places on the surface
where the coating is lacking, so both in the places
where the coating is porous and also there where no
coating is provided, there will be a conductive
resistant barrier layer of titanium oxide. Besides
no difficulties will be encountered in case the
coating is damaged. Furthermore it is possible to
provide the electrode with a fresh coating for a
substantially unlimited number of times if this is
considered necessary.

During the re-coating of the electrode the
barrier layer once formed remains intact. So far it
has been conventional to pickel such an electrode
after a certain number of hours during which it had
been operative, which resulted in losses of material.

An additional advantage of the present method
is that it is easy to deposit alloys of noble metals.
It also appears that the adherence of the coating
of noble metal to the titanium oxide will be stronger
owing to the roughness and especial structure thereof
than the adherence to the smooth surface of non-
oxidized titanium metal.

Example 1

A plate of titanium metal is thoroughly
degreased by rinsing it with e.g. petrol or carbon
tetra chloride. The plate is dried and placed as anode
between two graphite cathodes in a solution of 95 parts
by volume of concentrated phosphoric acid (98% or more)
and 5 parts by volume of concentrated nitric acid. The
voltage between the titanium anode and the graphite
cathodes is gradually raised to 100 volts, a barrier layer
of titanium oxide forming which also after the
termination of the electrolysis remains of excellent
quality.

On to the plate of titanium provided with said
electrolytically formed barrier layer a homogeneous
mixture is sprayed which is composed of

100 parts by volume of absolute ethanol

10 parts by volume of rhodium trichloride

2 parts by volume of coloured Venetian turpentine

5 parts by volume of hydrazine-mono hydrochloride.

When from the colour it appears that the entire
plate is covered by the mixture, the plate is dried and
the whole is heated in an open flame to a temperature
of at most 700°C. A rhodium coating of about 2 microns
5   will form.

The electrode thus manufactured is found to be
very satisfactury when used as anode for carrying out
electrolyses of all kinds of electrolytes, more
particularly also of baths containing chloride, with
10   the exception only of electrolyses evolving fluorine.
The allowable current density is 70 amperes per square
decimeter of higher.

Instead of the mixture mentioned above it is also
possible to apply by means of a brush mixture of
15   100 parts by volume of absolute ethanol
         10 parts by volume of platinum tetraiodide
         2 parts by volume of rhodium trichloride
         1 part by volume of lavendel oil
         3 parts by volume of colophonium resin
20   5 parts by volume of hydrazine.

By a careful heating an alloy of platinum and
rhodium will form on the barrier layer on the surface
of the titanium plate, which barrier layer is just as
satisfactory as a coating of rhodium only. In addition
the excessive potential of this electrode is appreciably
lower than of a similar electrode having a rhodium coating,
which leads to an economization in current.

Example 2

A rod of titanium is degreased in the manner
described in example 1 and placed for some hours in an
aqueous solution containing 30% of nitric acid to
remove foreign parts of metal which may be present on
the surface of said rod.

The rod is subsequently heated for two hours in
a current of air or oxygen at a temperature of $525^{\circ}C$
whereupon it is gradually cooled.

The rod thus provided with a barrier layer of
titanium oxide is coated with an extremely thin layer
of rhodium by means of the so-called electrolytic
brushing method.

To this end the titanium rod is connected to
the negative pole of a source of direct current, the
positive pole consisting of a core of carbon wrapped
in porous material such as wool or cotton wool, which
material is soaked in a alcoholic solution of a complex
organic rhodium compound, which solution also contains
a strong reducing agent e.g. hydrazine. If this moist
anode is pressed on to the titanium rod rhodium metal
will precipitate thereon.

This is partly the result of a normal electrolysis, while during the passage of the current through the alcoholic solution heat is liberated due to the high resistance, so that the volatile components evaporate and the hydrazine can exert its reducing action.

The precipitated rhodium will adhere particularly strongly to the barrier layer of titanium oxide, which barrier layer is not adversely affected by the conditions prevailing during the method described.

By moving the anode towards the portion of the rod where it is desired to obtain the coating of rhodium it is possible, for example, to coat the rod for three quarters of its length with rhodium. The remaining quarter need not be provided with a coating, because during the use of the rod as anode said remaining quarter is not submerged in the electrolyte. Because also said remaining quarter has its surface provided with a barrier layer of titanium oxide it is not possible for the titanium to be damaged by droplets of the electrolyte and the like.

The titanium rod thus treated is a very satisfactory anode for the electrolysis of alkali chloride solutions, oxidation of aldoses etc.

Example 3

Titanium gauze is degreased and purified in the manner as described in example 2. Subsequently the gauze is heated for three hours in an atmosphere of argon at a temperature of $1100^{\circ}C$. It appears that by this treatment the titanium oxide already present on the surface of the titanium metal is converted into a chemically more resistant layer which excellently protects the subjacent titanium, while the current is more easily conducted electronically, so that a layer of noble metal can be deposited thereon.

For this purpose the gauze is placed in a bath, containing an aqueous solution of $H6.PtC16,6H2O$. The gauze is connected to the negative pole of a source of direct current, a plate of platinum serving as anode. In order to prevent the barrier layer of titanium oxide on the titanium gauze being damaged by a strong evolution of hydrogen, the electrolysis is carried out at as low as possible a voltage. A suitable voltage is about 1.73 volts for a space of 3 centimeters between the electrodes. After six hours an extremely thin, well adhering layer of platinum has deposited.

The electrode thus manufactured is very well suited inter alia for the electrolytic preparation of persulphates, perborates etc.

661462

Example 4

A plate of titanium is pre-treated in the manner
as described in preceding examples. However, the
degreasing is effected more efficiently by condensing
vapour of the solvent on to the plate, so that at the
same time a smaller amount of solvent is necessary for
the degreasing operation.

The plate is subsequently placed for some hours
in an aqueous solution containing 20% of concentrated
sulfuric acid and 5% of hydrogen peroxide (30%) having
a temperature of 60°C. The plate is rinsed with hot
water and dried.

The plate now appears to be covered with a barrier
layer of titanium oxide which as excellent electronic
conductive properties, but which has a very high
resistance ionically. In the manner as described in
example 3 it is placed in the bath and connected to a
source of current. To the bath, however, hydrogen
peroxide or another oxidant is added which will bind the
hydrogen evolved so that the risk of the barrier layer
being damaged is reduced. In connection therewith a
voltage of 2.4 volts may be applied and already after
thirty minutes the plate is covered with a sufficient
amount of platinum.

Also the electrode thus manufactured is suited
for use as an anode for all kinds of electrolyses e.g.
in galvano plastics, in chromium baths, silver plating
baths etc.

Example 5

A plate of titanium is degreased and cleaned
in the manner described in example 2, whereupon it is
brushed one or a plurality of times with a solution
that is obtained as follows:

One gram of $PtCl_4.5H_2O$ is dissolved in 2 cc
of 100% ethanol, to which solution 10 cc of lavender
oil is added (Solution 1).

One gram of $IrCl_4$ is dissolved in 2 cc of
100% ethanol, to which solution 10 cc of lavender
oil is added (Solution 2).

The entire solution 1 is mixed with 4 cc of
solution 2, the mixture is heated in a flask
provided with a reflux cooler for at least one hour
at about $90°C$, but preferably longer and at any
rate so long that the vapour which all the same
escapes from the reflux cooler no longer has an
acid-reaction.

The cleaned plate of titanium is brushed
with the solution thus heated, whereupon the plate
is heated until the lavender oil has exerted its
reducing action (at about $400 - 600°C$), whereupon
a platinum-iridum alloy is found to have firmly
deposited on the titanium.

The adherence of the alloy to the titanium
may even be improved by quenching the plate in
cold water after the heating.

The electrode thus obtained is excellently suited for the electrolysis of hydrochloric acid solutions at a current density of 100 amp/dm^2 and a potential of 2.7 volts.

661462

all of this marked in black

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1.   A method of manufacturing an electrode, comprising, forming a core of titanium, oxidizing said titanium to form a barrier layer of titanium oxide on said core, and applying a coating of a noble metal or an alloy thereof on said barrier layer.

2.   A method, as defined in claim 1, wherein said barrier layer of titanium oxide is electrolytically applied to said core.

3.   A method, as defined in claim 1 or 2, wherein said barrier layer is electrolytically applied to said core at a voltage higher than the voltage which will normally be applied to said electrode when the electrode is used as an anode.

4.   A method, as defined in claim 1, wherein said barrier layer of titanium oxide is chemically applied to said core.

5.   A method, as defined in claim 1, wherein said barrier layer of titanium oxide is thermally applied to said core.

6.   A method, as defined in claim 1 or 5, wherein said barrier layer of titanium oxide is thermally applied to said core by heating said core in an oxidizing atmosphere at a temperature up to about 700°C.

7.   A method, as defined in claim 1, wherein said barrier layer of titanium oxide is chemically and thermally applied to said core.

14

B

8.   A method as defined in claim 1 and 5, wherein
said barrier layer is thermally applied to said core
in a weakly reducing atmosphere at a temperature greater
than 700°C.

9.   A method as defined in claim 1 or 5, wherein
said barrier layer is thermally applied to said core in
a neutral atmosphere at a temperature greater than 700°C.

10.   A method as defined in claim 1, 2, or 4, wherein
the coating of a noble metal or alloy thereof is applied by
galvanically depositing a coating of a noble metal or
alloy thereof over said barrier layer.

11.   A method as defined in claim 1, 2, or 4, wherein
said coating of noble metal or alloy thereof is applied by
chemically depositing a coating of a noble metal or alloy
thereof over said barrier layer.

12.   A method, as defined in claim 1, 2, or 4, wherein
said coating of noble metal or alloy thereof is applied over
said barrier layer by reduction of a solution containing
metal salts.

13.   A method of manufacturing electrode, comprising,
forming a core of titanium metal, placing said core as an
anode in an electrochemical apparatus containing a solution
of phosphoric acid and nitric acid between two spaced-apart
cathodes, passing current through said cathodes and said
core to form a barrier layer of titanium oxide on said core,
spraying a mixture containing a noble metal or alloy thereof
over said barrier layer, and subsequently heating said core
to a temperature of about 700°C to form a coating of a
noble metal or alloy thereof over said barrier layer.

14.   An electrode, comprising, a core of titanium metal having at its surface, a barrier layer, and a coating of a noble metal or alloy thereof substantially covering said barrier layer.

and this

SOM> (SUMMARY)

METHOD OF MANUFACTURING AN ELECTRODE COMPOSED OF A CORE OF TITANIUM AND A POROUS COATING OF A NOBLE METAL
H. B. Beer (Amalgamated Curacao Patents Co.)
Can. 661,462 - April 16, 1963

An electrode is formed as follows: A core of titanium is formed, then oxidized to form a barrier layer of titanium oxide on the core; a coating of a noble metal or an alloy of a noble metal is then applied on the barrier layer. The barrier layer of titanium oxide may be electro- lytically applied, chemically applied, or thermally applied. A combina- tion of these applications may also be used.
(13 method and 1 product claims) .

16

C

(ITEM G)

HEADINGS *
DISCUSSION NOT INPUT
EXAMPLES NOT INPUT
CLAIMS NOT INPUT

SUMMARY *

titanium core, noble-metal sheath. Barrier layer of
titanium oxide (where pores in n. metal) formed before
noble metal added.

I T E M·H

Erteilt auf Grund des Ersten Überleitungsgesetzes vom 8. Juli 1949
(WGBl. S. 175)

BUNDESREPUBLIK DEUTSCHLAND

AUSGEGEBEN AM
21. JUNI 1954

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DEUTSCHES PATENTAMT

PATENTSCHRIFT

Nr. 913 768

KLASSE 12h GRUPPE 2

D 11275 / IV b / 12h

Dr. Josef Müller, Rheinfelden (Bad.)
ist als Erfinder genannt worden

Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, Frankfurt/M.

Unlösliche Elektrode

Patentiert im Gebiet der Bundesrepublik Deutschland vom 1. Januar 1952 an
Patentanmeldung bekanntgemacht am 29. Oktober 1953
Patenterteilung bekanntgemacht am 13. Mai 1954

Die Erfindung betrifft unlösliche Elektroden, insbesondere unlösliche Anoden, bei elektrolytischen Prozessen, die aus mit Tantal in dichter Schicht überzogenen metallischen Formkörpern, vorzugs-
5 weise solchen aus Tantalmanteldrähten, bestehen und gegebenenfalls auch als Träger für eine Platinauflage dienen können.

Es ist bereits bekannt, bei elektrolytischen Prozessen, die an der Anode Platin als wirksame
10 Anodenfläche erfordern, das kostspielige Platin wenigstens zum Teil durch andere Metalle zu ersetzen, die einen erhöhten Übergangswiderstand aufweisen und bei anodischer Schaltung eine weitgehende Sperrwirkung besitzen. Aus diesem Grunde
15 hat man bereits Elektroden aus massivem Tantal verwendet, die auf ihrer Oberfläche entweder vollständig oder nur zum Teil mit einem Platinüberzug versehen waren. Solche Elektroden bestehen also

aus einer Kombination von viel Tantal und wenig Platin. Sie erfordern jedoch einen großen Aufwand 20
an dem teuren und außerordentlich schwer zu bearbeitenden Tantal. Außerdem ist die Leitfähigkeit des Tantals vergleichsweise gering, so daß in dieser Beziehung die elektrischen Eigenschaften nicht in allen Fällen genügen. 25

Gemäß der Erfindung bestehen nun die Elektroden aus Kombinationen von Tantal mit Metallen von hohem elektrischem Leitvermögen, in denen das Tantal nur eine verhältnismäßig dünne Oberflächenschicht bildet. Die neuartigen Elektroden nach der 30
vorliegenden Erfindung erfordern also nur einen außerordentlich geringen Aufwand an Tantal. Besonders vorteilhaft ist die Verwendung derartiger Kombinationen von Tantal mit anderen elektrisch gut leitenden Metallen in Form von Tantalmantel- 35
drähten von beliebigem Querschnitt, bei denen das

913 768

elektrisch gut leitende Metall den Kernwerkstoff und Tantal oder auch tantalhaltige Legierungen den Mantel bilden.

Für Prozesse, die als wirksame Elektrodenfläche
5 Platin erfordern, können derartige, mit Tantal überzogene Formkörper als Träger für eine Platinauflage dienen. Diese kann als geschlossener Überzug, beispielsweise elektrolytisch oder durch andersartige Abscheidung aus platinhaltigen Lösungen
10 oder Suspensionen, aufgebracht werden. Die Platinauflage kann dabei verhältnismäßig dünn sein und z. B. nur eine Stärke von 50 μ aufweisen, da die Funktion der Elektrode auch bei partieller Zerstörung der Platinschicht nicht nachteilig verändert
15 wird und das freigelegte Tantal infolge seiner hohen chemischen Indifferenz von dem Anolyten weder angegriffen wird, noch diesen in nennenswertem Maße zersetzt.

Erfindungsgemäß ist es jedoch auch möglich und
20 in vielen Fällen sogar sehr vorteilhaft, keine geschlossene Platinauflage zu verwenden, sondern das Platin etwa als Draht oder Spirale in Form einer Wicklung über den Träger, beispielsweise über den Tantalmanteldraht, zu legen.

25 Die Ausbildung der erfindungsgemäß aufgebauten Elektroden geht aus den schematischen Abb. 1 und 2 hervor, jedoch sind die möglichen Ausführungsformen nicht auf diese Beispiele beschränkt. Abb. 1 zeigt einen geraden Tantalmanteldraht mit Kupfer-
30 kern, der mit einem Platindraht bewickelt ist. Es ist dabei wesentlich, daß der Kernwerkstoff auch an der unteren, in dem Elektrolyt befindlichen Schnittfläche des Manteldrahtes mit Tantal überzogen ist. In der Abbildung bedeutet 1 den aus
35 einem elektrisch gut leitenden Metall wie Silber, Kupfer oder Aluminium bestehenden Kern des Manteldrahtes. Dieser ist mit einer Tantalauflage 2 allseitig und auch an der unteren Schnittfläche umgeben. Auf dem Tantalmantel befindet sich die
40 Platindrahtwicklung 3, die sich zweckmäßig etwa über $^9/_{10}$ der Gesamtlänge des Trägers erstreckt.

Um die Notwendigkeit der gesonderten Tantalauflage auf der mit dem Elektrolyt in Berührung stehenden Schnittfläche zu umgehen, kann es auch
45 zweckmäßig sein, gemäß Abb. 2 den als Träger dienenden Tantalmanteldraht U-förmig auszubilden und beide Enden aus dem Elektrolyt herauszuführen. Dabei kann der eine Schenkel gestreckt und der andere gegebenenfalls um diesen spiralig aufgewickelt sein. Auch in dieser Abbildung bedeutet
50 1 den Kernwerkstoff, 2 den Tantalmantel und 3 den aufgewickelten Platindraht, der seinerseits entweder glatt oder als Spirale oder als Mehrfachwendel aufgelegt werden kann.

Für Prozesse, bei denen möglichst gering dimen-
55 sionierte Anoden verwendet werden müssen, kann als Anode z. B. ein Silber-Tantalmanteldraht mit einem Gesamtdurchmesser von 1,3 mm und einer Tantalauflage von 100 μ dienen, der bei 1 m Gesamtlänge auf einer Länge von 90 cm mit einem
60 Platindraht von 0,15 mm Durchmesser und 10 m Länge gewickelt ist. Eine solche Elektrode erfordert einen Einsatz von 10 g Silber, 6,3 g Tantal und 3,78 g Platin.

Die erfindungsgemäß aufgebauten Anoden be-
65 nötigen also einen geringen Aufwand an kostspieligen Metallen und vereinigen die vollständige chemische Indifferenz und die ausgezeichnete elektrolytische Sperrwirkung der Tantaloberfläche mit der optimalen Leitfähigkeit des Kernwerkstoffes, z. B.
70 des Silbers oder Kupfers. Sie haben sich für alle mit unlöslichen Anoden arbeitenden elektrolytischen Prozesse, insbesondere für elektrolytische Oxydation, hervorragend bewährt und sind mit Vorteil, vor allem bei der Herstellung von Perverbin-
75 dungen, z. B. Überschwefelsäure oder ihren Salzen, Perborat oder auch Perchlorat, verwendbar.

PATENTANSPRÜCHE:

1. Unlösliche Elektrode, insbesondere für die
80 elektrolytische Oxydation, z. B. für die Herstellung von Perverbindungen, bestehend aus einem mit einer geschlossenen, dünnen Schicht Tantal oder tantalhaltiger Legierung überzogenen Grundkörper aus elektrisch gut leiten-
85 dem Metall, z. B. Silber, Kupfer oder Aluminium.

2. Elektrode nach Anspruch 1, zusätzlich über der Tantalschicht mit einer dünnen Schicht Platin überzogen oder mit dünnem Platindraht,
90 gegebenenfalls in Form einer Spirale, umwickelt.

3. Elektroden nach Anspruch 1 oder 2, gekennzeichnet durch ihre Herstellung aus Tantalmanteldraht.

Hierzu 1 Blatt Zeichnungen

SUMMARY

Abstract for Ger. 913,768

Metal-Brine-Electrode
Silver, copper, or aluminum is coated with tantalum. The tantalum coating may be, in turn, coated with platinum. A platinum wire or a tantalum wire may be wound around the electrode.
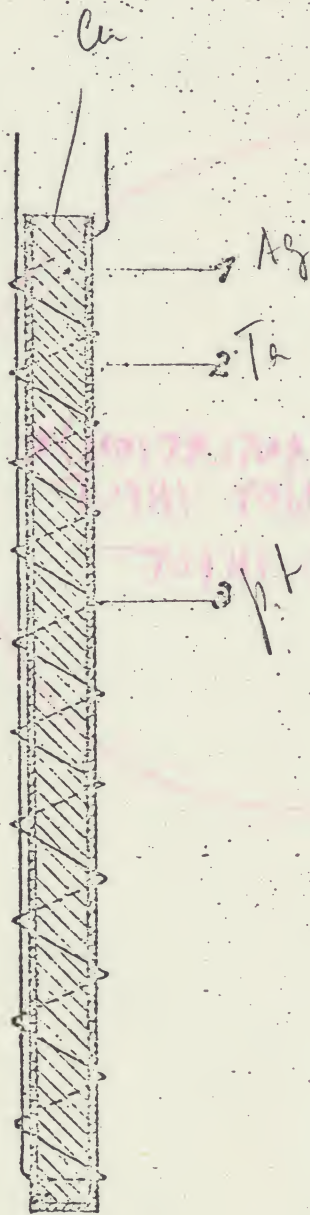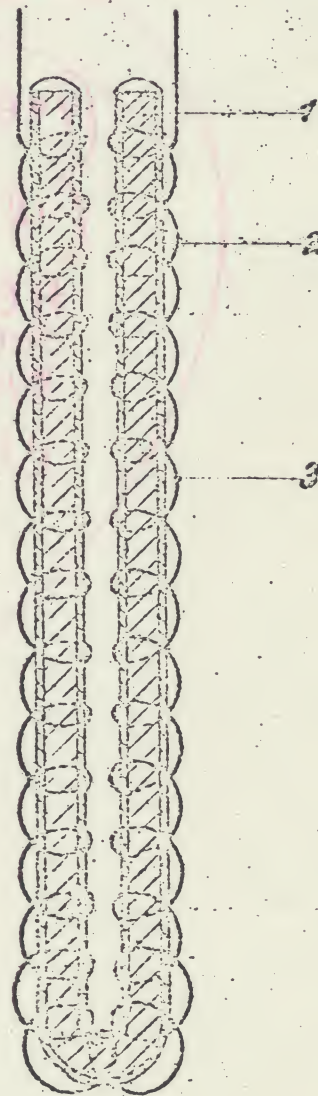
Cu

1 Ag

2 Ta

3 Pt

1

2

3

Abb. 1

Abb. 2

(ITEM 4)

(IN GERMAN)

HEADINGS*
SUMMARY (TRANSLATION)*
DISCUSSION - NOT INPUT

CLAIMS NOT INPUT

Silver/copper/aluminum coated w/R titanium & perhaps platinum.
Possibly wound a wire around it.

Improvements in or relating to anodes.

COMPLETE SPECIFICATION

We, N.V. Curacaosche Exploitatie Maatschappij Uto, a limited liability Company, of Willemstad, Curacao, Netherlands Antilles, 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:—

As is known, anodes for carrying out electrolyses and other electrochemical processes frequently consist of a precious metal, e.g. platinum. Such anodes are quite satisfactory but their high cost constitutes a bar to their being used on a large scale.

In this connection the term precious metal is meant to include platinum, ruthenium, rhodium, palladium, osmium, iridium and gold, and alloys essentially composed of one or more of these metals.

In order to obviate this drawback it is possible to use an anode consisting of a core of a less expensive or base metal coated with a layer of precious metal, generally platinum. In some cases said layer need only be extremely thin and it may then be applied, for instance, electrolytically. Good results, however, are only obtained if the core metal, in places where the layer of precious metal is porous, is provided after coating with an inert barrier layer.

Thus anodes which consist of a core of tantalum coated with platinum, or a core of zirconium or a zirconium alloy coated with platinum have been proposed. In both cases the platinum coating may be applied electrolytically. Another example is an electrode of bismuth coated with a layer of platinum.

The fact that such electrodes have a high anodic contact resistance must be based on the fact that during the passage of the current the base metal of the core is coated with an inert barrier layer in those places where said metal may come into contact with the electrolyte owing to the porosity of the coating, which barrier layer is not easily attacked by the reaction medium and cannot dissolve therein either. Such a barrier layer consists of a non-porous film which protects the subjacent base metal against the electrolyte and which generally speaking does not allow the current to pass.

It has now been found that titanium is particularly suited to be used as a core metal for an anode because it has been discovered that titanium is not only capable of forming a barrier layer in aqueous solutions of substantially all electrolytes, whereas other metals such as bismuth, tantalum and zirconium will only do this if oxygen is evolved directly at the anode, but because when using titanium in addition a very stable barrier layer is formed which is very resistant and which upon prolonged use continues to perform its function in contradistinction to the above mentioned known anodes, the barrier layer of which is less resistant and will soon decompose in various kinds of electrolytes, e.g. in those containing halides.

The invention consists in an anode having a core of titanium and a coating of a precious metal as hereinbefore defined, a protective barrier layer of titanium oxide being formed beneath the coating at such places where it is porous.

The barrier layer may be formed *in situ* e.g. in the electrolytic bath, in which the coated electrode is to serve as anode, or the barrier layer may be applied to the core metal by a further treatment after said core metal is coated, before it is put into service as an anode.

The barrier layer may be formed by the electrolysis of a solution of an acid, a base or a salt, including electrolytes containing halide ions, with the exception, however, of fluorides.

The barrier layer is preferably applied by a treatment before use. It is preferable to

form the barrier layer at a higher voltage than that to which the anode will be subjected in ordinary use. This will ensure that the barrier layer will remain intact in use.

5   For elucidating the invention two examples are subjoined.

EXAMPLE 1

If titanium is introduced into an aqueous solution of chloride, e.g. in hydrochloric
10 acid and the titanium is connected as anode the passage of current will be reduced to substantially zero within a few seconds because the titanium is coated with a protective layer which renders any further passage
15 of current impossible and fully protects the subjacent material. If a plate of titanium is coated with a layer of rhodium having a thickness of 1 micron, and if said plate of titanium thus coated is again connected as
20 anode in a hydrochloric acid solution the passage of current will continue undisturbed while the pores in the rhodium are not harmful to the subjacent titanium because this is protected by the film of oxide which
25 will be locally formed. Said electrode is pre-eminently suited for the electrolysis of alkali chloride solutions because there is no question here of wear and tear, the current density may be several times larger than in
30 the case of the known electrodes, and there is no pollution of the electrolyte, so that there is a considerable economy in costs of maintenance.

In addition a much greater number of
35 electrodes may be placed in a certain space in the bath because in comparison with the thick graphite or magnetite electrodes the diameter of the electrode according to the invention is appreciably smaller. Because
40 in the alkali chloride electrolysis a continuous movement of the bath is of great importance said electrodes may be perforated, if desired, so that a high rate of flow can be obtained.

45 EXAMPLE 2

The electrode of titanium described in example 1 and coated with a layer of rhodium of 1 micron can also be used for the electrolysis of salt melts. To this end the
50 electrode is arranged in an aqueous solution of 20% hydrochloric acid and is connected as anode, while a plate of carbon serves as cathode. The voltage between said two electrodes is gradually raised to 150 Volts
55 (direct current voltage) and is maintained at said level until in the porous places the plate of titanium is coated with a barrier layer through which substantially no current will pass any longer.
60 This electrode is placed in a melt of zinc

chloride which is heated at 330°C and subsequently the plate is connected as anode and a plate of carbon is used as cathode. When the passage of current is sufficient the mixture will remain at the melting tem- 65 perature without external heating, while in the case of an insufficient passage of current heat is to be supplied from the outside. Chlorine will evolve at the anode and zinc will deposit on the cathode. It is possible 70 in this manner to obtain very pure zinc.

Similarly, this anode can also be used for other salt melts. The use of titanium as a core metal is extraordinarily attractive in this because the melting temperature of 75 titanium is in the neighbourhood of 1800°C and that of rhodium upwards of 1900°C. By means of this electrode therefore it is possible to work at very high temperatures without the anode being damaged. The 80 carbon graphite electrodes conventionally used for this purpose are much more sensitive to temperature and in consequence will be subjected to an appreciable wear.

WHAT WE CLAIM IS: 85

1. An anode having a core of titanium and a coating of a precious metal as hereinbefore defined, a protective barrier layer of titanium oxide being formed beneath the coating at such places where it is porous. 90

2. A method of making an anode as claimed in claim 1, in which the barrier layer is formed electrolytically after the precious metal coating is applied.

3. An anode made by the method of 95 claim 2.

4. A method of carrying out electrolysis of an aqueous electrolyte containing chlorine ions or a salt melt, using an anode as claimed in claim 1 or 3.   100

5. A method as claimed in claim 4, using an anode as claimed in claim 3, in which the operating voltage is lower than that used for the formation of the barrier layer.   105

6. An anode substantially as described in either of the examples 1 and 2 given.

MARKS & CLERK.

(ITEM A)
HEADINGS *
DISCUSSION *
EXAMPLES **
CLAIMS *

Titanium node with oxide barrier layer
at exposed parts.

United States Patent Office

3,103,484
Patented Sept. 10, 1963

1

3,103,484
ANODES FOR ELECTROLYTIC CHLORINE EVOLUTION
Georg Messner, Milan, Italy, assignor to Oronzio de Nora Impianti Elettrochimici, Milan, Italy, a corporation of Italy
No Drawing. Filed Oct. 4, 1960, Ser. No. 60,307
3 Claims. (Cl. 204—290)

This invention relates to novel anodes comprised of platinum or titanium-platinum coated with a layer of magnetite which has an empirical formula of Fe_3O_4.

The production of chlorine has become very important in the chemical field and the trend in chlorine manufacture in the United States and Europe is more and more to the use of the mercury cell. In a typical horizontal mercury cell there is a bed of slowly flowing mercury and disposed thereover are anodes approximately 2 mm. away from the mercury to form an amalgam and is later decomposed brine is run into the cell on top of the mercury. When an electric current is passed throught the cell, chlorine is liberated at the anode and the sodium is absorbed in the mercury to form an amalgam and is later decomposed in the presence of water to form sodium hydroxide.

The anodes are usually made of graphite. However, the graphite is rather rapidly consumed and frequent, cumbersome and time-consuming readjustment of the electrodes is necessary in order to maintain the proper electrode distance. Also, carbon dioxide formed from the decomposed graphite is evolved with the chlorine and has to be separated from the chlorine. Therefore, graphite anodes are not too desirable.

Anodes of platinum metals such as platinum, iridium and rhodium, or alloys of these metals, have also been used. These anodes are better than the graphite anodes as no carbon dioxide is formed to interfere with the chlorine gas. Also, the platinum type anodes are not consumed as rapidly as graphite and therefore do not have to be readjusted frequently.

The platinum-type anodes have disadvantages, however. After only a short period of anode operation, the potential of the platinum-type anodes is increased and there is an increased energy consumption in the electrolytic process. Furthermore, while the platinum-type anodes are not consumed as rapidly as graphite, there is depletion of the anode on the order of 1 to 3 grams of metal per ton of chlorine produced. Due to the high cost of the platinum-type metals, this adds a substantial expense to the operation of the mercury cell.

Anodes composed of iron or steel as a base and coated with magnetite as a protection against erosion are known. However, the coefficient of expansion of magnetite relative to the iron or steel base is so different that the adhesive bond between the magnetite and the base metal is broken and the magnetite layer flakes off from the base metal which is then depleted. The exposure of the base metal may lead to serious consequences in the cell operation.

It is an object of the present invention to obtain a platinum type anode which is not consumed in the production of chlorine in a mercury cell.

It is another object of the invention to obtain a mercury cell anode which has a low single potential.

It is another object of the invention to obtain a titanium-platinum-magnetite anode which results in a reduction in the amount of platinum needed for the anode.

It is a further object of the invention to produce a novel platinum type anode by coating a platinum-type metal with a layer of magnetite which has the empirical formula of Fe_3O_4.

These and other objects and advantages will become more obvious from the following detailed description.

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The anodes of the present invention consist of platinum-type metals covered by a layer of magnetite. The anode base need not consist entirely of the platinum-type metal. A base metal such as titanium or tantalum coated with a thin layer of a platinum-type metal may also be used so that there is a reduction in the amount of platinum needed for the anode. Due to the expense of tantalum, titanium coated with a platinum-type metal is preferred.

Titanium or tantalum covered with magnetite cannot be satisfactorily used as an anode although they are effective conductors of electricity. When the iron on titanium or tantalum is oxidized to form the magnetite covering, the oxidation is either incomplete or carried out too far. If incomplete, not all the iron will be oxidized to magnetite and the unoxidized iron will dissolve in the mercury cell and the magnetite coating will chip off. If the oxidation is carried too far, the titanium or tantalum will be oxidized to titanium dioxide or tantalum dioxide, respectively, which are non-conductors of electricity. This problem does not occur in the platinum-type metal-magnetite, tantalum-platinum-type metal-magnetite or titanium-platinum-type metal-magnetite anodes as the platinum-type metals are not affected by the oxidation.

The anodes of the present invention overcome the disadvantages of the previous electrodes. No carbon dioxide is formed which would complicate the recovery of chlorine gas. The magnetite coating prevents depletion of the anode, and the use of platinum-type metals, tantalumplatinum-type metals or titanium-platinum-type metals as the core of the anode produces an anode with a low single potential. By the use of titanium or tantalum coated with a thin layer of platinum as the base metal, a substantial reduction in the amount of platinum needed for the anode is obtained.

One way of applying the magnetite coating to the platinum anode is to form a thin layer of iron or an iron alloy on the platinum-type metal and then oxidize the iron. The layer of iron may be formed electrolytically, with a metal spray gun, by dusting, or any other manner. The iron layer is oxidized by heating the anode in an atmosphere of a mixture of an inert gas such as argon or helium and carbon dioxide, air, water, or diluted oxygen at a temperature between 600° and 900° C. to produce a magnetite layer which adheres firmly to the platinum-type metal. Instead of diluting the oxidizing atmosphere with an inert gas, reduced pressures, preferably 200 to 600 mm. Hg, may be used.

The magnetite layer may also be applied by depositing iron compounds, such as the hydroxide of bi- or tri-valent iron, iron carbonate, iron oxalate, or any other iron compound which decomposes upon being heated to temperatures of 600° to 900° C. and which may be transformed into a compound corresponding approximately to Fe_3O_4 by the presence of an oxidizing atmosphere such as that described above. The iron compounds may be deposited on the platinum-type metal by chemical or electrophoretic precipitation or by mechanical spraying, rolling or painting on the platinum-type metal.

Particularly well adhering magnetite coatings are those which are obtained by at least slightly diffusing the iron layer in the platinum-type metal layer prior to oxidation, for example, by a heat treatment in an inert atmosphere at a temperature between 700° and 900° C., preferably 800° C. In those cases where iron compounds are applied to the platinum-type metal, the layer is treated under reducing conditions prior to the heat treatment for the purpose of diffusion, for example, by passing a dry stream of hydrogen over the iron compound layer at elevated temperatures. After transformation of the iron compound into the magnetite, the magnetite layer can be

made still more resistant against wear by a subsequent heat treatment.

In the following examples there are described several preferred embodiments to illustrate the invention. However, it should be understood that the invention is not intended to be limited to the specific embodiments. While the specific examples use only platinum or titanium-platinum as the base metal, any one of the platinum metals or alloys or mixtures thereof may be used with equal success. The platinum metals include osmium, rhodium, iridium, rhenium, ruthenium, palladium and masurium as well as platinum.

Example 1

A metal sheet made of platinum which has the final shape of an anode and is provided with perforations or slits is electrolytically coated in an iron sulfate bath with a layer of 0.020 mm. of iron. After washing and drying, the coated sheet is heated in an atmosphere consisting of about 50% CO_2 and 50% argon for one hour at 800° C. and is then allowed to cool in an atmosphere of argon.

A dark violet oxide layer is formed which, in the role of an anode, evolves chlorine in a NaCl solution having a sodium chloride content of 300 grams per liter with no attack of the platinum taking place. The single potential of the anode during continuous electrolysis in sodium chloride solution and a current density of 30 amperes per dm.² is 0.4 volt lower than the single potential of a platinum sheet under an identical load. The wear of the active magnetite layer is so low that the anode remains operative over about one year. At the end of a year's operation, the platinum base may be cleaned and recoated as described above.

Example 2

A piece of metal mesh made of titanium sheet 2 mm. thick is coated with a platinum layer of about 0.005 mm. thickness. An iron layer of 0.02 mm. thickness is applied to this platinum layer in a vacuum by means of a cathode spray. Thereafter, the coating is heated in an inert atmosphere of argon for one-half hour at 800° C. and is then treated in a gas atmosphere consisting of approximately 10% H_2O, 30% CO_2 and 60% argon for one hour at 700° C. The metal mesh is allowed to cool in a dry argon atmosphere. The magnetite layer thus produced protects the platinum from depletion during anodic chlorine production and exhibits a lower anodic single potential than platinum metal. It is advantageous to apply a heat treatment at 900° C. in an inert atmosphere, either in a vacuum or in a noble gas atmosphere, subsequent to the oxidation at 700° C.

Example 3

An iron layer of about 0.1 mm. thickness is sprayed with the aid of a spray gun upon a perforated platinized titanium sheet 2 mm. thick, and the resulting sheet is heated for two hours in a pure, dry atmosphere of argon at 900° C. and is then oxidized for two hours at 650° C. in a dry mixture consisting of about 50% CO_2 and 50% pure argon. The treated sheet is allowed to cool in a dry atmosphere of argon. The operation may be repeated if a thicker magnetite layer is desired.

Example 4

A perforated sheet of platinum 2 mm. thick is provided with an iron layer of about 0.025 mm. thickness by electroplating means, heated in vacuo for 30 minutes at 750° C.,

then oxidized in an atmosphere of 50% argon and 50% CO_2 for one hour at 650° C., again provided with a layer of iron 0.025 mm. thick by electroplating means, and again oxidized in the same manner.

The treated sheet is allowed to cool in a vacuum. Depending upon the desired life of the anode, this process may be repeated in order to obtain a correspondingly thick layer of magnetite.

Example 5

A layer of iron 0.025 mm. thick is dusted in a vacuum on a perforated sheet made of platinum, CO_2 gas corresponding to about 300 mm. Hg is then introduced for about one hour during which the sheet is heated to about 650° C. Thereafter, the dusting of iron in a vacuum is repeated until an additional 0.025 mm. of iron have been deposited, which is then again oxidized into magnetite as already described. This cycle is repeated until the desired thickness of the magnetite layer is reached. Thereafter, the coated platinum sheet is allowed to cool in argon. The anode produced in this manner has an increased life as a chlorine-evolving anode in aqueous solutions of chloride.

Example 6

A layer of iron about 0.02 mm. thick is applied by electroplating means to a sheet made of platinum provided with slit-like apertures and the iron coated sheet is oxidized at 650° C. in an atmosphere composed of CO_2 and argon. A layer of iron approximately 0.1 mm. thick is then applied to the magnetite layer by means of a metal spray gun, and this iron layer is oxidized in a CO_2-argon atmosphere at 650° C. for two hours. The treatment can be repeated until the desired thickness of the magnetite layer is reached.

Various modifications of the products and the process of the present invention may be made without departing from the spirit of this invention or the scope thereof, and it is to be understood that the invention is limited only as defined in the appended claims.

I claim:

1. An electrolytic anode consisting of a base metal selected from the group consisting of titanium and tantalum, a thin adherent coating of a platinum metal on said base metal, and an exterior thin adherent coating of magnetite over said platinum metal coating.

2. The electrolytic anode of claim 1 in which the coating of platinum and the coating of magnetite is on an anodically active surface only of said base metal.

3. An electrolytic anode consisting of a base metal selected from the group consisting of titanium and tantalum, a thin adherent porous coating of a platinum metal on said base metal, and an exterior thin adherent porous coating of magnetite over said platinum metal coating.

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(handwritten annotations) EX, REF, SUM (SUMMARY)

An electrolytic anode for uses such as producing chlorine electrolytically is made up of a base metal such as titanium or tantalum, a thin coating of a platinum metal on the base metal, and an exterior thin coating of magnetite over the platinum metal coating.

(3 PRODUCT CLAIMS)

(ITEM E)
HEADINGS *
DISCUSSION *
EXAMPLES * * * * *
CLAIMS *
REFERENCES *
SUMMARY *

Titanium or titanium base, platinum coat

Titanium or titanium base, platinum coat

1

3,234,110
ELECTRODE AND METHOD OF MAKING SAME

Henri Bernard Beer, Schiedam, Netherlands, assignor to Amalgamated Curacao Patents Company N.V., Curacao, Netherlands Antilles, a corporation of the Netherlands Antilles
No Drawing. Filed Apr. 23, 1964, Ser. No. 362,180
Claims priority, application Netherlands, Feb. 6, 1959, 235,848
8 Claims. (Cl. 204—38)

The present invention relates to an electrode having a base or core of titanium or titanium with small amounts of alloying metals therein, which core is covered with a barrier layer of titanium oxide and coated with a noble metal coating, and to a method of producing such an electrode.

This application is a continuation-in-part of my application Serial No. 6,351, filed February 3, 1960, now abandoned.

In several of my prior copending applications, there has been disclosed an electrode particularly suitable for use as an anode which has such a core or base of titanium, either substantially pure titanium or titanium with small amounts of alloying metals therein, and a coating of a noble metal, such as platinum, iridium, rhodium, or alloys of these metals. In making such electrodes, the core of titanium is treated so as to remove any oxide coating therefrom and the noble metal coating is formed thereon. Since such coatings are at best slightly porous, there are places in the coating at which the titanium core is exposed. At these pores there is formed a barrier layer of titanium oxide. This barrier layer is formed by placing the electrode in an electrolyte and electrolytically forming the barrier layer. Alternatively, the barrier layer can be formed by a chemical and/or a thermal treatment which makes a more stable and chemically inert barrier layer than forming the barrier layer electrolytically.

During the use of such electrodes as anodes in such electrolytical processes as, for example, brine electrolysis, or as anodes in cathodic protection arrangements, ionic current flow can take place through the noble metal coating and electronic current flow will take place from the noble metal coating to the titanium core. The barrier layer over the titanium core which is exposed through the pores in the noble metal coating will prevent ionic current flow directly to the titanium core, and will thereby prevent a chemical attack by the electrolyte, which is usually quite corrosive on the titanium of the core. In addition the noble metal coating is chemically resistant so that the titanium core is protected from chemical attack where it is coated by the noble metal.

When the noble metal coating is damaged during electrolysis so that the bare titanium of the core is exposed, an electrolytically formed barrier layer will be produced over the exposed area, but there will be a short period of time when the titanium is exposed to attack by the electrolyte, and this is detrimental to the life of the electrode.

I have now discovered that the titanium or titanium alloy core of such an electrode can be entirely covered with a barrier layer of titanium oxide, and thereafter coated with a noble metal coating, and it will still act as an electrode, particularly as an anode in electrolytic processes such as, for example, brine electrolysis, and as an anode in cathodic protection methods. The existence of a barrier layer of titanium oxide between the noble metal coating and the titanium core or base does not interfere with the electronic flow of current from the noble metal coating to the titanium base, while at the places where the noble metal coating is imperfectly formed or has pores in it, the barrier layer prevents ionic flow of current from the electrolyte to the titanium base.

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This characteristic is generally not true of the other so-called film forming metals, i.e. the metals which have their surfaces easily oxidized by contact with the air. When these metals are coated with an oxide film, the film offers great resistance to both ionic current flow, i.e. flow of current from an electrolyte into the metal itself, an electronic current, i.e. flow of current from a conducting metal which is in metal to metal contact with the film forming metal. Thus, an electrode having a core of aluminum which has been oxidized in air or has been intentionally provided with a layer of oxide for example by anodizing, and which has been coated with a noble metal, offers a high resistance to the passage of electric current from the noble metal coating to the aluminum core.

The electrode according to the invention is particularly valuable in that if, during use, the noble metal coating should be damaged, for example by peeling off, there will be a barrier layer already formed beneath the noble metal coating which will immediately resist attack by the electrolyte, and the electrode will accordingly be preserved and its life extended.

It is therefore an object of the present invention to provide an electrode particularly suitable for use as an anode which has a core or base of titanium or titanium with small amounts of alloying metals therein, a barrier layer of titanium oxide covering said core or base, and a noble metal coating over the barrier layer, the noble metal being taken from the group consisting of platinum, rhodium, iridium, and alloys of these metals.

It is a further object of the present invention to provide a method of making an electrode particularly suitable for use as an anode by forming a barrier layer of titanium oxide on such a core or base, and then coating a noble metal over the barrier layer, the noble metal being taken from the group consisting of platinum, rhodium, iridium, and alloys of these metals.

As already indicated, the core or base can be substantially pure titanium, or it can have small amounts of alloying metals therein. For example, the titanium can have vanadium or aluminum therein in an amount up to 4% by weight, or it can have zirconium therein up to 10% by weight. These percentages of metals other than titanium will not inhibit the film forming characteristic of the titanium. Accordingly, where reference is made to a core or base of titanium in this specification, it is to be understood that such a core or base includes a base of substantially pure titanium as well as a base of titanium and an alloying metal as herein described.

By the term "barrier layer" as used to describe the oxide layer formed on the titanium core of the electrode of the present invention, is meant a layer of oxide which resists attack by the electrolyte in which the electrode is used, and at the same time prevents passage of current directly from the electrolyte to the titanium core but permits passage of current from the noble metal coating to the core.

In connection with the following examples, it is essential to understand that in forming the barrier layer on the titanium core by placing the core in an electrolyte as an anode and passing a current through it, the voltage which is impressed on the core must be below the breakdown voltage for titanium in the electrolyte in question. Otherwise, if the breakdown voltage for titanium in the particular electrolyte is exceeded, the form of oxide which will be produced is not that which produces a barrier layer, but rather is one which, when it is coated with a conducting metal, will not permit electronic current conduction therethrough from a noble metal coating to the titanium core at the normal operating voltages of the electrodes during their use in electrolysis.

It is further necessary to understand that the breakdown voltage will vary depending on the particular electrolyte in which the barrier layer is being formed on the titanium core, and in fact the breakdown voltage will be further dependent on the metal of the core, should it be, for example, an alloy of titanium. For this reason, in the examples, the voltages at which the barrier layer is formed can vary from example to example. However, for purposes of illustration, it can be mentioned that the voltage for forming the barrier layer herein should not exceed 10 volts, when the electrolyte is aqueous sodium chloride. With oxalic acid or tartaric acid the voltage for forming the barrier layer may amount up to 35–40 volts. When these voltages are exceeded in the electrolyte indicated, the oxide layer on the core loses its ionic resistance and its electronic resistance is very substantially increased to the point where the resulting product, when coated with noble metal, is not effective for the uses described. In the usual operations according to the invention, the voltage utilized will amount to 5 to 60% of the breakdown voltage depending on the concentration and temperature of the electrolyte.

The method of making the electrodes according to the invention comprises at least partially immersing a core of titanium in an electrolyte, impressing a voltage on said core, which voltage is below the breakdown voltage for titanium in said electrolyte, but sufficient to form a barrier layer of titanium oxide on the portion of the core which is immersed in the electrolyte, painting a solution of at least one salt of a noble metal taken from the group consisting of platinum, rhodium and iridium or alloys thereof in an organic volatile solvent onto the barrier layer thus formed on said core, heating said painted core to evaporate the volatile solvent, and then firing the core in an atmosphere for converting the deposited salt to metal.

The method will now be set forth in detail in connection with the following examples. In these examples, a plurality of specimens of substantially pure titanium plate each 1 cm. x 2 cm. were prepared according to the conditions set forth in Table I, there being used 100 cc. of electrolyte in each instance, and the electric power being supplied from an accumulator at the indicated voltages which are below the breakdown voltages for titanium in the respective electrolytes.

plates were heated in air at a temperature of 250° C. for 11 minutes to evaporate and burn off the solvent. After the last application of the paint and the heating in air, the painted plates were each heated in a closed furnace in an atmosphere of ammonia and a reducing gas, for example illuminating or lighting gas, at a temperature of 330° for 10 minutes in order to form on the plates a coating of a platinum and iridium alloy without adversely affecting the underlying barrier layer of titanium oxide. Thereafter the plates were gradually cooled.

The thus treated specimens 1, 3, 5 and 6 were then used as anodes in the electrolysis of 30% brine solutions at a temperature of 60° C. and a current density of 1500 amperes per square meter, at an applied voltage of 2.8 volts. The anodes performed excellently, and at a low and constant overvoltage this current density could be maintained. Specimens 2 and 4 were used as anodes in a similar chloride alkali electrolysis with excellent results.

Examples 7–12

Specimens 7–12 were each coated four times with a paint which contained 2 grams of rhodium in the form of a rhodium compound, for example rhodium chloride, per 10 cc. of organic solvent, for example ethanol. After each coating the plates were heated in air at a temperature of 250° C. for 10 minutes to evaporate and burn off the solvent. After the last application of the paint and the heating in air to evaporate and burn the solvent, the painted plates were each heated in air at a temperature of 650° C. for 10 minutes in order to form on the plates a coating of metallic rhodium. Thereafter the plates were gradually cooled.

The thus treated specimens were then used as anodes in oxidation processes, such as the production of perborates, persulphates, and the like, and were also used in alkaline electrolytes. They were economical to use and were mechanically very strong.

Examples 13–18

Specimens 13–18 were each coated twice with a paint which contained 10% by weight platinum chloride, 20% of an ethereal oil (lavender) and the remainder an organic diluent, for example acetone and isopropyl alcohol. After each coating the plates were heated in air at 390° C. for 1 minute to evaporate and burn off the solvent, and

TABLE I

Specimen	Volt.	Immediately after voltage is applied		After 15 minutes		Electrolyte aqueous solution	° C.	Resistance across barrier or oxide layer in ohms
		Intensity in microamperes	Ionic resistance in ohms	Intensity in microamperes	Ionic resistance in ohms			
1	4	36,000	111	57	70,250	1% NaCl	20	0.001–0.005
2	6	100,000	60	160	37,500	5% NaCl	20	0.001–0.005
3	6	25,000	240	115	52,700	1% NaCl	20	0.001–0.005
4	4	45,000	89	80	50,000	1% H₂SO₄	20	0.001–0.005
5	4	100,000	40	100	40,000	10% H₂SO₄	50	0.001–0.005
6	4	115,000	35	130	30,800	10% NaOH	20	0.001–0.005
7	6	50,000	120	130	46,200	1% NaCl	20	0.001–0.005
8	4	45,000	89	75	53,300	36% NaCl	20	0.001–0.005
9	4	50,000	80	45	88,900	5% NaCl	40	0.001–0.005
10	4	100,000	40	100	40,000	10% H₂SO₄	20	0.001–0.005
11	4	90,000	44	90	44,500	5% NaOH	20	0.001–0.005
12	4	34,000	118	20	200,000	10% tartaric acid	20	0.001–0.005
13	4	55,000	73	85	47,100	5% NaCl	20	0.001–0.005
14	6	100,000	60	140	42,800	36% NaCl	20	0.001–0.005
15	4	15,000	267	85	47,100	1% NaCl	40	0.001–0.005
16	4	100,000	40	70	57,200	5% H₂SO₄	20	0.001–0.005
17	4	60,000	67	85	47,100	1% NaOH	20	0.001–0.005
18	4	300,000	13	15	267,000	10% oxalic acid	20	0.001–0.005
19	4	60,000	67	55	72,750	1% NaCl	80	0.001–0.005
20	4	75,000	53	55	73,750	5% NaCl	80	0.001–0.005

Examples 1–6

Specimens 1–6 were each coated four times with a paint which contained 1 gram of platinum in the form of a platinum salt, for example platinum tetraiodide, and 0.03 gram of iridium in the form of an iridium salt, for example iridium tetrachloride, per 10 cc. of an organic solvent, for example ethanol. After each coating the

to deposit a layer of metallic platinum on the barrier layer on the titanium cores. Thereafter the platinum coated titanium electrodes were heated in air at 350° C. for 48 hours.

The thus treated specimens were used as anodes in the cathodic protection of ships, piers and the like in sea water, and proved very satisfactory.

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Example 19

A plate of substantially pure titanium was partly coated with platinum, and was at least partially immersed as an anode in an electrolyte which was an aqueous solution having 5% NaCl at a temperature of 70° C. so that at least part of the platinum coated portion of the electrode was in the electrolyte. A voltage of 4 volts was applied to the electrode to form a barrier layer on the uncoated portions of the electrode which were immersed in the electrolyte. Immediately after the application of the voltage, the current intensity was 1,000,000 microamperes and the ionic resistance was 4 ohms. After the voltage had been applied for 15 minutes, the current intensity was still 1,000,000 microamperes and the ionic resistance was still 4 ohms. A barrier layer was formed on the uncoated parts of the electrode which had a resistance as measured across the barrier layer of 0.001–0.005 ohm.

The portions of the plate which had the barrier layer formed thereon were subsequently coated with platinum, and the thus formed electrode was used as an anode with excellent results.

Example 20

A plate of titanium metal is thoroughly degreased by rinsing it with e.g. petrol or carbon tetrachloride. The plate is dried and placed as anode between two graphite cathodes in a solution of 95 parts by volume of concentrated phosphoric acid (98% or more) and 5 parts by volume of concentrated nitric acid. The voltage between the titanium anode and the graphite cathodes is gradually raised to 100 volts, a barrier layer of titanium oxide forming which also after the termination of the electrolysis remains of excellent quality.

On to the plate of titanium provided with said electrolytically formed barrier layer a homogeneous mixture is sprayed which is composed of

100 parts by volume of absolute ethanol,
10 parts by volume of rhodium trichloride, .
2 parts by volume of colored Venetian turpentine,
5 parts by volume of hydrazine-monohydrochloride.

When from the color it appears that the entire plate is covered by the mixture, the plate is dried and the whole is heated in an open flame to a temperature of at most 700° C. A rhodium coating of about 2 microns will form.

The electrode thus manufactured is found to be very satisfactory when used as anode for carrying out electrolyses of all kinds of electrolytes, more particularly also of baths containing chloride, with the exception only of electrolyses evolving fluorine. The allowable current density is 70 amperes per square decimeter or higher.

Instead of the mixture mentioned above it is also possible to apply by means of a brush mixture of

100 parts by volume of absolute ethanol,
10 parts by volume of platinum tetraiodide,
2 parts by volume of rhodium trichloride,
1 part by volume of lavender oil,
3 parts by volume of colophonium resin,
5 parts by volume of hydrazine.

By the method according to the invention there has been produced an electrode in which there is a barrier layer completely covering the titanium of the base, so that where there are pores or breaks in the noble metal coating on the electrode, the titanium of the base is protected by the barrier layer. Should the coating peel or otherwise be removed, all that is exposed is the barrier layer, the titanium of the core being protected from attack by the electrolyte in which the electrode is immersed.

In addition, it is possible with this type of electrode to provide the electrode with a fresh coating of noble metal a substantially unlimited number of times, if desired. The barrier layer remains intact once it has been formed, so that it is not necessary to pickle the electrode before applying a new noble metal coating, as has heretofore

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been done with this type of electrode. Moreover, there will be no loss of the core material during recoating, since the noble metal is simply added to the barrier layer covered core.

A further advantage of the electrodes according to the invention is that the adherence of the coating of noble metal is enhanced because the surface of the oxide barrier layer is rougher than the surface of the bare titanium metal.

It is thought that the invention and its advantages will be understood from the foregoing description and it is apparent that various changes may be made in the method without departing from the spirit and scope of the invention or sacrificing its material advantages, the forms of the method hereinbefore described and set forth in the examples being merely preferred embodiments thereof.

I claim:

1. An electrode, comprising a core of a metal taken from the group consisting of titanium and an alloy of titanium and small amounts of alloying metals, a high ionic resistance, low electronic resistance barrier layer of titanium oxide covering at least a part of said core, and a noble metal coating over said barrier layer, the noble metal being selected from the group consisting of platinium, rhodium, iridium, and alloys thereof, said barrier layer being electrolytically deposited on said core by impressing thereon a voltage below the breakdown voltage of the metal of the core in the electrolyte used for the formation of the barrier layer.

2. An electrode, comprising a core of a metal taken from the group consisting of titanium and an alloy of titanium and small amounts of alloying metals, a high ionic resistance, low electronic resistance barrier layer of titanium oxide covering at least part of said core, and a noble metal coating over said barrier layer, the noble metal being selected from the group consisting of platinum, rhodium, iridium, and alloys thereof, said barrier layer being electrolytically deposited on said core by impressing thereon a voltage below the breakdown voltage of the metal of the core in the electrolyte used for the formation of the barrier layer, and the noble metal coating being deposited on the barrier layer by painting onto the barrier layer a solution containing a compound of the noble metal and evaporating the solvent.

3. An electrode as claimed in claim 2 in which the alloying metals are taken from the group consisting of up to 4% vanadium, up to 4% aluminum, and up to 10% zirconium.

4. An electrode, comprising a core of a metal taken from the group consisting of titanium and an alloy of titanium and small amounts of alloying metals, a barrier layer of titanium oxide covering at least a part of said core, and a noble metal coating over said barrier layer, the noble metal being selected from the group consisting of platinum, rhodium, iridium, and alloys thereof, said barrier layer having an electronic resistance in the range of about 0.001 to 0.005 ohm and an ionic resistance of at least about 35,000 ohms which is formed by immersing the core in a sodium chloride electrolyte for about 15 minutes with an impressed voltage of about 4 volts.

5. A method of making an electrode, comprising the steps of immersing at least a part of a core of a metal taken from the group consisting of titanium and an alloy of titanium and small amounts of alloying metals in an electrolyte as an anode, impressing a voltage on said core, which voltage is below the breakdown voltage for titanium in said electrolyte, to thereby form a high ionic resistance, low electronic resistance barrier layer of titanium oxide on the immersed part of said core, and then coating over said barrier layer a noble metal taken from the group consisting of platinum, rhodium, iridium, and alloys thereof.

6. A method of making an electrode, comprising the steps of immersing at least a part of a core of a metal taken from the group consisting of titanium and an alloy

of titanium and small amounts of alloying metals in an electrolyte as an anode, impressing a voltage on said core, which voltage is below the breakdown voltage for titanium in said electrolyte, to thereby form a high ionic resistance, low electronic resistance barrier layer of titanium oxide on the immersed part of said core, and then painting onto said barrier layer covered core a solution containing a compound of a noble metal taken from the group consisting of platinum, rhodium, iridium, and alloys thereof, and heating the painted core for evaporating the solvent and converting the compound to a metallic coating while retaining the barrier layer undisturbed.

7. A method as claimed in claim 6 in which the painted core is heated in air for evaporating and burning the solvent, and then is heated in a reducing atmosphere for reducing the compound of the noble metal while leaving the barrier layer unaffected.

8. A method of making an electrode, comprising the steps of partly coating a core of a metal taken from the group consisting of titanium and an alloy of titanium and small amounts of alloying metals with a noble metal, immersing at least a part of the core including a part of the noble metal coated portion in an electrolyte as an anode, impressing a voltage on said core, which voltage is below the breakdown voltage for titanium in said electrolyte, for forming a high ionic resistance, low electronic resistance barrier layer of titanium oxide on the immersed part of said core which is uncoated with the noble metal, and then coating over said barrier layer a noble metal taken from the group consisting of platinum, rhodium, iridium, and alloys thereof.

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WINSTON A. DOUGLAS, *Primary Examiner.*

JOHN H. MACK, *Examiner.*

HEADINGS *
DISCUSSION *
EXAMPLES *****
REFERENCES * ! AM
~~REFER~~

[hpnt to live reference]

Long-life electrods having an oxide film between
titanium/tantalum core and noble metal coating. The oxide film
not reducing current flow. the barrier layer prevents corrosion to the core.

July 28, 1953   J. BURNHAM   2,647,079

PRODUCTION OF INSULATED CONDENSER ELECTRODES

Filed June 3, 1948

INVENTOR = JOHN BURNHAM
TITLE = PRODUCTION OF INSULATED CONDENSER ELECTRODES
DATE OF FILING = ~~18 SEPT 19~~ 28 JULY 1953
COMPANY = SPRAGUE ELECTRIC COMPANY
U.S. PATENT 2, 647, 079
(ITEM C)

POLYTETRAHALO-
ETHYLENE

OXIDE FILM

FILM FORMING
METAL (Al, Ta, Ti)

JOHN BURNHAM
INVENTOR.

BY Arthur G. Connolly
his attorney

This invention relates to insulated electrical conductors and more specifically refers to insulated condenser electrodes and electrical condensers employing same.

The use of formed oxide films on aluminum in electrostatic condenser constructions is well known in the art. Despite the volume of references describing such films and condensers, there has been no commercial success with condensers of this type. This may be attributed to several disadvantages inherent in prior procedures and structures. First, the oxide films are relatively fragile and difficultly handled without damaging the insulation. Second, it has been difficult to adequately provide insulation within the cracks and weak spots of the oxide film. In the manufacture of electrolytic condensers, such weak spots are overcome by the forming of additional oxide film during the aging or use of the condenser. This self-healing feature is not possible in electrostatic condensers. Other disadvantages have resulted from the inability to operate the condenser electrodes at very high temperatures, eliminating some of the possible advantage of an aluminum oxide film over organic dielectric materials.

It is an object of the present invention to overcome the foregoing and related disadvantages. A further object is to produce new and improved insulated electrical conductors which are particularly applicable in the manufacture of electrical condensers. Additional objects will become apparent from the following description and claims.

These objects are obtained in accordance with the invention where there is produced an insulated conductor selected from the class containing aluminum, tantalum and titanium, the surface of said metal being provided with an adherent porous film of the oxide of the metal, the pores of said oxide film being impregnated with a polytetrahaloethylene resin. In a restricted sense, the invention is concerned with an insulated condenser electrode comprising aluminum on the surface of which is an adherent porous aluminum oxide film, the pores of which are impregnated with particles of a polytetrahaloethylene resin. In one of its preferred embodiments, the invention is concerned with an insulated condenser electrode comprising aluminum, on the surface of which is an adherent porous aluminum oxide film between about 1.0 micron and about 400 microns in thickness, the pores being impregnated with polytetrafluoroethylene particles. The invention is also concerned with novel methods for producing the insulated conductors of the invention.

I have discovered that highly useful and desirable insulated conductors may be produced with film forming metals, such as aluminum, titanium and tantalum, by a true impregnation of the pores of the oxide film with a polytetrahaloethylene resin. In contrast to prior so-called dry oxide films, my insulation is durable, tough, non-inflammable and may be operated at extremely high temperatures. According to my invention, the base electrode is treated to produce an oxide film thereon by electrolytic methods and prior to drying of the film is subjected to a treatment with a suspension of polytetrahaloethylene resin particles. These particles are deposited in the pores of the oxide film and are subsequently sintered to produce a dielectric of heretofore unobtainable properties.

The metals which may serve as base electrodes in accordance with my invention include aluminum, titanium and tantalum. These are provided with a porous oxide film by anodic treatment in an appropriate electrolyte. The pores in the film generally extend perpendicularly to the plane of the base metal surface. Representative electrolytes are oxalic acid, citric acid, boric acid, chromic acid and the like. Where high porosity is desired on aluminum, for example, I prefer to form an oxide on the metal in an oxalic acid electrolyte. For very high voltage films, I prefer to form a porous oxide film on the metal from an oxalic acid electrolyte and subsequently form a less porous oxide film thereon from a boric acid electrolyte. As a general rule, the formation in the oxalic acid electrolyte should be conducted between about 2 volts and about 600 volts. The boric acid film formation process may be conducted at voltages up to about 1800 volts. Prior to drying of the oxide film, the treatment with the resin particles is carried out as described below. It is, however, desirable to wash the residual electrolyte from the film with water or a solvent for the electrolyte.

The resin is polytetrahaloethylene resin or a copolymer of a tetrahaloethylene with another polymerizable material. Representative resins are polytetrafluoroethylene, polytrifluorochloroethylene, polytetrachloroethylene and the like. These may be suspended in water or other medium by use of an appropriate suspension agent, or polymerized in the presence of the medium. The suspension medium should be compatible with the electrolyte solvent, for example, when

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a water solution of oxalic acid is used as the electrolyte and water is used as the washing medium, the suspending medium for the resin particles should be water or a water-soluble material to insure thorough impregnation of the pores of the coating. The metal with its undried oxide film thereon is passed through a suspension of resin particles, then dried and subjected to a temperature sufficient to cause sintering of the resin particles together.

The temperature for the particle sintering depends, of course, upon the particular resin employed. In the case of polytetrafluoroethylene the temperature is preferably between about 350° C. and 425° C. The electrode is thereby insulated for high voltages, is durable and tough, is resistant to moisture and common solvents, and will not sustain flame.

The invention will be further described with reference to the appended drawing which shows a cross-section of an insulated conductor. The base metal is provided with a porous oxide film corresponding to the underlying metal. The pores of the oxide film are impregnated with the resin, in the form of sintered particles. If so desired, the resin may be provided in excess, for example, by a multiple treatment to form a continuous, impervious top coating, thus increasing the electrical breakdown voltage. The dielectric constant of the oxide is greater than that of the resin and it is often desirable to limit the thickness of the top coating of resin.

Conductors insulated in accordance with the invention are particularly useful in the manufacture of electrical condensers. Two electrode foils, at least one of which is insulated as described above, may be stacked or rolled in the usual manner to produce an extremely durable high-temperature condenser. For high voltage applications, it is desirable to employ initially thicker oxide films, and then to treat them in accordance with the invention. If so desired, the surface of the insulated conductor such as shown in the figure may be provided with a metal coating, such as evaporated, sprayed or mechanically deposited silver, zinc, copper and the like, to produce an integral electrode and thus a complete condenser section.

The invention is, of course, applicable to many other devices, such as insulated wires, insulated electrical structural members, corrosion resistant mechanical assemblies and the like.

It is contemplated that the impregnation of the pores may be accomplished by drying the oxide film and heating the assembly to a high

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temperature, e. g. 300° C. or higher, thus expanding and driving out much of the air filling the pores. The assembly may then be quenched in the suspension of resin particles, drawing them into the pores. Thereafter, the film may be dried and the resin particles sintered as heretofore described.

As many widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claims.

I claim:

1. A process for producing insulated condenser electrodes which comprises anodically oxidizing a foil of a metal selected from the class consisting of aluminum, tantalum and titanium in a film forming electrolyte to form on the foil a porous oxide film having a thickness of from 1 to 400 microns, washing the porous oxide film with a liquid which is a solvent for the electrolyte to flush away the electrolyte, contacting the washed and undried film with a suspension of particles of a polytetrahaloethylene resin in a vehicle soluble in the washing liquid to impregnate the pores of the film with such resin particles, drying the impregnated film and sintering the resin particles together.

2. A process as claimed in claim 1, wherein the resin is polytetrafluoroethylene, the washing liquid and suspension vehicle are both water, and the sintering is carried out at temperatures between about 350° C. and 425° C.

3. A process as claimed in claim 1, wherein the porous oxide film is formed on an aluminum foil by first electrolyzing the latter in an oxalic acid electrolyte and then in a boric acid electrolyte.

JOHN BURNHAM.

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(item c)
HEADINGS *
DISCUSSION *
CLAIMS *
REFERENCES *

Production of an insulated (capacitive) ~~conit~~ conductor by creation of a porous oxide coating on aluminium, tantalum & titanium; coating it with resin.

COMPLETE SPECIFICATION

Improvements in or relating to Electrodes

We, N.V. Curacaosche Exploitatie Maatschappij Uto, of Handelskade 24, Willemstad, Curacao, Netherlands Antilles, a Company registered under the Laws of the Netherlands Antilles, 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:—

In co-pending Patent Application No. 10872/58 (Serial No. 855,107) an electrode is described which consists of a core of titanium provided with a coating of a precious metal, which core is provided with a barrier layer of titanium dioxide in those places where the coating is porous.

Said barrier layer may be applied electrolytically before the electrode is put into use.

Throughout this specification and claims, by the term " noble metal " is meant a metal selected from a list comprising gold and the metals of the platinum group, viz., platinum, ruthenium, rhodium, palladium, osmium and iridium.

In this specification and claims the expression " core " is intended to cover not only the case where the titanium is completely surrounded with noble metal, but also cases in which the titanium is only partially surrounded, e.g. a layer coated on only one side.

It has now been found that such an electrolytically formed barrier layer is not always satisfactory because the ohmic resistance of the titanium is so many times greater than that of the noble metal that, especially in the fine pores, insufficient energy can be supplied to build up a barrier layer which provides sufficient chemical protection. This is especially to be expected when using electrolytes which together with the titanium will produce compounds which produce the oxide forming the barrier layer only after hydrolysis. Examples of such electrolytes are hydrohalic acids or salts thereof. The fact has been established that owing to the absorptive capacity of the fine pores in the coating there is a possibility that the concentrated anolytes will accumulate in said pores so that the base core or carrier metal may be chemically attacked.

Furthermore, it has been found in actual practice that the barring effect of an electrolytically formed barrier layer needs to be built up again to a slight extent each time when the current is switched on again after being switched off. It will be found that after switching off the current the ohmic resistance in the reverse (non-conducting) direction of the layer has dropped to below the value that is desired. This desired minimum, however, will be reached again in a few seconds after the current has been switched on. The explanation of this phenomenon is presumably to be found in the fact that an electrolytically built up barrier layer has a slight excess of oxygen in its lattice, which oxygen gets lost when the current is interrupted, so that the resistance of the layer decreases. (The more oxygen there is bound to the material of the barrier layer, the greater will be the resistance). The supply of current, however, will soon replenish the amount of oxygen lost.

For the correct operation of the electrode this change of the resistance and the concomitant change of the chemical resistance during the rest pauses may be dangerous as it will make the electrode vulnerable.

These disadvantages of electrolytically formed barrier layers may be eliminated by using a barrier layer of titanium oxide formed or strengthened by a heat treatment of the electrode in any oxygen containing atmosphere. It is then also possible to provide the smallest pores with a protective layer.

A layer formed according to the invention will impart, through the pores of the conducting noble metal coating, an absolute resistance

[Price 3s. 6d.]

against substantially all chemical substances to the titanium. The barrier layer thus formed is not porous either. This effect can be achieved by forming the compounds at such a temperature that the layer will sinter to a degree so that its surface will close. A closed layer thus sintered cannot be obtained by electrolysis alone. In addition the adherence of this layer to the metal may even be improved by gradually cooling the electrode after the formation of the protective layer.

When the current is interrupted the ohmic resistance, which is related to the chemical resistance, does not decrease to any significant extent. Also when the oxide of the metal is formed the oxygen is found to adhere strongly to the metal.

The thermal treatment may cause the oxide formed to sinter and thus to adhere better. Furthermore gases adsorbed on one of the metals e.g. after the cathodic precipitation of the noble metal coating, may be expelled by the thermal treatment, so that they can no longer exert a harmful influence. Another effect of the thermal treatment may reside in the conversion of the oxide into another more desirable crystal form. Thus it has been found, for example, that the titanium dioxide formed by heating titanium in the presence of air will change into the rutile form when it is subjected to a further heating treatment, which rutile form is chemically the most resistant one. In some cases an extremely thin layer of oxide is already present on the metal as commercially available, which oxide is only converted into another, more stable form by the thermal treatment.

The resistant coating of noble metal may be applied to the titanium in various known manners. This may be effected by electroplating or chemical deposition, cathodic sputtering, rolling or by ultrasonically welding of extremely thin foils. It is also possible to start from an extremely thin foil of noble metal and electrolytically to apply thereto a layer of titanium, which subsequently is brought into the desired inert condition according to the invention in the places where the noble metal is porous. The non-coated side of the titanium is also rendered entirely inert during this treatment.

When using titanium as a core or carrier metal, it is possible, for economic reasons, to precipitate a thin layer thereof on iron, e.g., electrolytically and to rhodanize this iron-titanium. By heating the electrode in an atmosphere of oxygen the titanium will flow about the iron so that no pores are left in the titanium, while at the same time the oxide of titanium is formed in the place where the rhodium coating is porous.

The electrodes manufactured according to the invention may be used for carrying out electrolyses both in aqueous solutions and in organic electrolytes in the heat or in the cold.

They may also be used for electrolysing salt melts.

The invention will be further elucidated with reference to the following examples. Said examples, however, should not be taken as limiting the invention in any respect.

EXAMPLE 1

A plate of titanium was degreased in petrol. Subsequently it was pickled for one minute in a solution of 60 parts by weight of water, 20 parts by weight of nitric acid and 3 parts by weight of sodium fluoride at 50° C., rinsed with clean water and suspended for 10 minutes in a solution of 80 parts by weight of (100%) acetic acid and 20 parts by weight of ammonium bifluoride. The plate was then connected to a source of alternating current, a plate of titanium being used as the other electrode. The voltage of this alternating current was raised to 10 volts and subsequently the first mentioned plate was taken out of the solution, rinsed well and galvanically rhodanized in a conventional bath. The plate of titanium was covered then with an extremely thin, but strongly adhering layer of rhodium.

Subsequently it was introduced for four minutes into an atmosphere of helium at 400—500° C. as a result of which the rhodium adhered better to the titanium. Subsequently the plate was cooled and kept in an oven at a temperature of 800° C. in air or in another mixture richer in oxygen for 15 minutes, so that the titanium changed into titanium dioxide in the porous places. Subsequently the plate was slowly cooled in the same atmosphere. The electrode obtained was excellently suited for use in acid, neutral or alkaline electrolytes.

EXAMPLE 2

A plate of titanium was coated with rhodium in the manner already described. Subsequently it was placed as an anode in an electrolyte consisting of 80% by weight of phosphoric acid, 10% by weight of sulphuric acid (98%) and 10 parts by weight of water. A plate of lead was used as cathode and the voltage gradually raised to 10 volts. A layer of titanium oxide formed in the pores of the noble metal on the titanium. The treatment took about 10 minutes. The plate was rinsed well, dried and subsequently placed in an oven in which the temperature is raised to 800° C. After this temperature had been maintained for one minute the oven was allowed to cool gradually. Care was taken that during the heating fresh air was unable to enter the oven. Subsequently the plate was taken from the oven and was then ready for use. The heat-treatment of the oxide first obtained electrolytically resulted in a layer which was much more resistant than the layer formed electrolytically.

It will be understood that while the examples relate to the use of rhodium, similar methods may be used for the application of a coating of the other noble metals listed, and the invention is also applicable to the formation of barrier layers under such coatings when they are porous.

WHAT WE CLAIM IS:—

1. An electrode consisting of a core (as hereinbefore defined) of titanium and a coating of a noble metal, characterized in that the titanium in the places where it is not fully coated by the noble metal has a barrier layer of titanium oxide formed or strengthened thereon by a heat treatment of the electrode in an oxygen-containing atmosphere.

2. An electrode according to Claim 1, characterized in that the barrier layer consists of titanium oxide in the rutile form.

3. An electrode according to either of Claims 1 or 2, characterized in that the thermal treatment is carried out in such a manner that the compound formed will sinter and coalesce.

4. An electrode when made substantially as described in either of the examples given.

5. A method of making an electrode substantially as described with reference to either of the examples given.

MARKS & CLERK.

(ITEM F)

HEADINGS ✳

BEGINNING ✳

EXAMPLES ✳ ✳

CLAIMS ✳ → P.3

Titanium electrode coated with oxide barrier layer
and noble metal outside. Oxide ~~later~~ is in gaps of n. metal

THE SWISS CONFEDERATION

CONFEDERATE PATENT OFFICE

PATENT

Published July 16, 1923

No. 100171 (Application filed: June 12,1922, 6:30 P.M.)

Class 36 h

ORIGINAL PATENT

CHEMISCHE FABRIK WEISSENSTEIN, Gesellschaft m. b. H.,
Weissenstein ob der Drau (Kärnten, Austria)

Anodes for the production of per compounds.

In order to avoid using anodes of pure platinum in
electrolysis, the procedure was to cover tantalum in the form of
wire or sheet metal electrolytically with platinum in such a
way that the entire tantalum surface received a continuous
coating of platinum, so that it was impossible for the electrolyte
to come in contact with the tantalum foundation. For short-
time use of such platinum-plated anodes for analytical purposes,
they have rendered good service. However, when attempts were made
to use such anodes in continuous operation for the production of
per compounds, they showed little durability; a part of the
platinum coating adhered to the foundation, while another part

had so little adhesiveness that after being used for a short
time in electrolysis the platinum particles gradually passed
into the electrolyte.

Surprisingly, the electrolysis for the purpose of
producing per compounds could nevertheless be carried on with
such a damaged electrode, as long as just enough of the platinum
was still in sufficient contact with the foundation to bring
about passage of the current. However, a continuous operation
with an electrode in this condition is obviously not feasible,
especially since a reduction in the contact surface between the
tantalum and the platinum results in an increased voltage, a
                        current yield,
reduction in the electrolytic efficiency, and thereby an increase
in the cost of production.

What is most surprising is the discovery that the
appearance of the tantalum surface either as metal or in the
oxidized state does not exert the slightest harmful influence on
the process of formation and on the stability of the formed
per compounds. This behavior of the per compounds, which are
otherwise so extremely sensitive to metal-containing catalysts,
now offers the possibility of producing very stable and durable
electrodes.

To produce such a platinum overlayer on a tantalum
foundation that it does not cover the entire tantalum surface with
platinum, is technically considerably simpler and cheaper to
detach
loosen than encasing the entire tantalum body with the expensive
                        overlayer
platinum. The superimposed layer can, for example, be carried out
by electrolysis or by hammering on, welding on, rolling on, etc.

PATENT CLAIM:

Anode for the production of per compounds, characterized by the feature that the anode consists of tantalum, the surface of which is only partly provided with a platinum coating.

CHEMISCHE FABRIK

WEISSENSTEIN

Gesellschaft m. b. H.

Representative: A. RITTER, Basel.

NP

(ITEM B)
HEADINGS
DISCUSSION
CLAIMS

platinum-covered tritium electrode
~~tritium-cove~~ which is not completely covered.