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ELECTRODE.

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To all whom it may concern:

Be it known that I, COLIN G. FINK, a citizen of the United States, residing at Yonkers, in the county of Westchester, State of New York, have invented certain new and useful Improvements in Electrodes; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains, to make and use the same.

This invention relates to an improved electrode of particular value for use as an anode in the electro-deposition of copper from copper sulfate electrolytes, but available for use for other purposes.

For efficient and satisfactory use in the electrolytic recovery of copper from copper sulfate electrolytes, an anode should possess certain properties. In the first place, it should be of the so-called "insoluble anode" type, that is to say, it should be to a high degree insoluble in the electrolyte, or in other words, it should possess high resistance to anodic disintegration. In addition, the anode should have high electrical conductivity and a low anodic potential in order to maintain the electrical losses as low as practicable. And again, the anode should be of such a character as to permit the ready discharge of oxygen gas therefrom, thereby eliminating or minimizing the undesirable consequences of polarization. In practice, it is generally only possible to approximate the ideal condition with respect to each of the aforementioned properties, and, accordingly, it is necessary in the production of an anode for commercial practice to resort to a compromise of the ideal conditions with respect to these properties in order to obtain an anode possessing the desired properties to a more or less satisfactory degree.

The present invention contemplates the provision of an improved anode possessing in a remarkably satisfactory degree the aforementioned desirable properties. Thus, the anode of the invention is highly resistant in anodic disintegration, and, in addition, has a low anode potential and good electrical conductivity. Moreover, in its preferred form, the anode possesses to a satisfactory degree depolarizing characteristics permitting the free discharge of oxygen gas from its surface.

In its broad aspect, the invention contemplates the provision, as a new article of manufacture, of an electrode resistant to anodic disintegration and made up of an alloy containing cobalt and silicon. A depolarizing ingredient, such as manganese, is preferably included in the alloy, and, as a result of electrolytic action, provides a depolarizing coating or film for the surface of the electrode which facilitates the discharge of oxygen gas therefrom. A hardening agent is also preferably included in the alloy and serves the purpose of hardening the surface coating or film of the depolarizing agent. Chromium may be advantageously used as the hardening agent, and I have found that tungsten, molybdenum and uranium may also be used as the hardening agent. Throughout the specification and the appended claims, I have mentioned manganese with the intention of defining any equivalent depolarizing ingredient and similarly I have mentioned chromium with the intention of defining any equivalent hardening agent.

The improved electrode of the invention is accordingly made up of an alloy of which the principal constituents are cobalt and silicon. In its preferred form, the electrode also contains manganese and chromium, together with a certain amount of carbon. I have secured excellent results with an alloy of the following composition: 11.5 to 13% silicon, 4 to 6% manganese, 4 to 6% chromium, 0.8 to 1.2% carbon, and the balance cobalt. If desired, 5 to 30 parts of the cobalt content of the alloy may be replaced by manganese, or 5 to 12 parts of the cobalt content may be replaced by chromium, or 5 to 8 parts of the cobalt content may be replaced by nickel, without objectionably altering the advantageous properties of the alloy as an anode material.

As the result of my investigations and researches, I have found that an improved electrode, resistant to anodic disintegration in the electro-deposition of copper from copper sulfate electrolytes, and in particular, cop-

per sulfate electrolytes containing chlorides and nitrates, can be produced from cobalt and silicon, by combining these metals in the form of a cobalt-silicon alloy of appropriate composition. I have also found that when cobalt and silicon are appropriately alloyed together with a small amount of manganese and carbon, the resulting alloy shows a marked resistance to such anodic disintegration and has greater strength and other desirable qualities which adapt it particularly for use as an insoluble anode in the electrodeposition of copper from sulfate solutions. I have, moreover, found that the addition of chromium, or other equivalent metal of the chromium group such as tungsten, molybdenum or uranium, to the alloy imparts to the electrode further advantageous characteristics which will be more particularly mentioned hereinafter.

I have found that commercial cobalt is well adapted for use in the production of electrodes in accordance with the principles of the invention. Cobalt has a marked affinity for carbon and, if desired, may be preliminarily combined with the amount of carbon to be incorporated in the anode alloy. The proportion of carbon, of manganese, of chromium, and of silicon can be somewhat varied, but in general neither the carbon, the manganese, the chromium or chromium group metal, nor the silicon should be too low, or the corrosion of the anode will be objectionably increased. On the other hand, the carbon, the manganese, the chromium and the silicon content should not be too high. A high silicon content results in a decrease in the strength of the anode and an increase in both its tendency to corrode and in its specific electrical resistance. If the carbon content is too high, the carbon separates out in a graphitic form. I have obtained the best results with a carbon content slightly in excess of the amount which can be combined, so that there is a small amount of fine graphitic carbon, such as will give a grey surface to the fracture, but without any excess of graphitic carbon.

I have found that the alloys of cobalt and silicon are distinguished from alloys of other more or less similar metals with silicon in their availability for use as electrodes. This distinction, and the advantages of the cobalt-silicon alloys, are due in part, I believe, to the anodic properties of the cobalt, that is, to its tendency to be deposited on the anode, which distinguishes cobalt from most other metals which deposit on the cathode. The advantageous properties of the cobalt alloys are further due, as I believe, to the peculiar characteristics of the cobalt-silicon alloys. Microphotographs of cobalt-silicon, alloys containing about 12 to 15 percent of silicon indicate that the silicon is in part present as such or in solid solution in the cobalt, while a large part is present in the form of a eutectic made up of a solid solution of cobalt silicide (Co_2Si) in the cobalt and perhaps also of the cobalt silicide itself. The microphotographs indicate that the resistance to corrosion may be largely due to the presence of the silicon and of the cobalt silicide.

With anodes of cobalt-silicon alloys and copper cathodes I have found a voltage in dilute sulfuric acid of about 1.7 to 2.0 volts at a current density of 20 amperes per square foot of anode surface and a spacing of $1\frac{1}{2}$ inches between anode and cathode. I have furthermore found a maximum strength against flexure to be obtained with a silicon content of about 12 to 15%. For example, a flexure strength of around 6200 pounds per square inch (unit beam 1 inch square, 12 inch span) has been possessed by electrodes of this silicon content. Both any material increase and any material decrease in the silicon content of the alloy seems to decrease the mechanical strength of the electrode, and in general, the greatest strength is obtained at between 12 and 15% of silicon. In its breaking strength, the improved electrodes of the invention are to be distinguished from electrodes of iron and silicon, where, for example, a similar content of silicon gives an electrode with a flexure strength of about 1000 to 1500 pounds per square inch. The greater strength of the cobalt-silicon electrodes of the invention, as compared, for example, with iron silicon electrodes, enables a much thinner anode to be employed without objectionable reduction in strength, so that less space is occupied thereby in the electrolytic tanks or cells. Any considerable increase in the silicon content of the cobalt-silicon electrodes, as above noted, tends to increase both the voltage and the brittleness.

I have obtained good results with a carbon content of about 1%, or between 0.5% and 1.2%, and with a silicon content of from 12 to 15%. Graphitic carbon, as above pointed out, is objectionable beyond a certain small amount, but inasmuch as cobalt will combine more readily than iron with a small amount of carbon, it is possible to include such a larger amount without an objectionable amount of graphitic carbon being present.

From investigations which I have made of microphotographs of electrodes embodying the principles herein disclosed, I believe the improved electrode of the invention owes its advantageous properties to the fact that it is composed, for the major part, of two constituents. The first of these constituents is more or less soluble in the copper sulfate electrolyte, but possesses good electrical conductivity. The second con-

stituent is relatively insoluble in the electrolyte, but is not a good conductor of electricity. The aforementioned first constituent appears to be an alloy or a mixture of alloys of the various metallic constituents of the electrode, while the aforementioned second constituent appears to be a eutectic, probably silicide of cobalt. It furthermore appears from the microphotographs that the structure of the anode is made up of particles of the aforementioned first constituent (an alloy of good electrical conductivity but relatively soluble in the electrolyte), which particles are more or less enclosed or enveloped with a coating of the second constituent (the eutectic which is relatively insoluble in the electrolyte but of poor electrical conductivity). The eutectic, accordingly, appears to provide a coating for the alloy particles which effectively serves to prevent these particles from going into solution at an objectionably high rate, but at the same time this eutectic coating is so shallow or narrow as not to objectionably decrease the electrical conductivity of the electrode as a whole.

The cobalt-silicon anode of the invention is of special advantage in sulfate electrolytes containing appreciable amounts of nitrates and chlorides. In such electrolytes lead anodes disintegrate rapidly. Lead anodes stand up more or less satisfactorily in sulfate electrolytes free of nitrates or chlorides, but even in such electrolytes the cobalt-silicon anode of the invention is superior to lead anodes, since the anode of the invention possesses a higher current efficiency than a lead anode and stands up better in all electrolytes including those for which lead is adapted.

I have found the improved electrode of the invention of particular value when employed as an anode in the electro-deposition of copper from such solutions as are obtained upon leaching Chuquicamata copper ores. This electrolyte contains primarily copper sulfate, sulfuric acid, and a number of other salts among which are included alkali nitrates, sulfates, chlorides and iron sulfates. In addition, the electrolyte may contain small quantities of aluminum, calcium, magnesium and potassium sulfates.

With an anode of the preferred composition hereinbefore mentioned, I have found that the loss in electrodes of this character at 20° C. and at 20 amperes per square foot of anode surface, is approximately 0.5 pounds per one hundred pounds of copper deposited, and that the voltage from anode to cathode at this temperature is about 1.9 volts. I have found that higher temperatures give lower corrosion losses, which is in contradistinction to the behavior of ferro-silicon anodes.

The manganese included in the improved electrode serves the purpose of a depolarizer. In an acid sulfate electrolyte at a temperature of from 10 to 15° C., the manganese goes into solution as permanganic acid. At temperatures of from about 30° C. to 60° C., this permanganic acid formation is practically absent and instead there is obtained a heavy deposit of manganic oxide on the surface of the anode. In both cases, however, manganese dioxide is precipitated or deposited on the anode, but in the case of the warm or heated solution, the deposit of manganese dioxide is more adherent and there is practically no loss of manganese in the solution. This deposit of manganese dioxide, together with some cobalt oxide, on the anode acts as a depolarizer, as will be well understood by those skilled in the art, and insures the free discharge or liberation of oxygen gas from the surface of the anode. Moreover, I have found that cobalt-silicon anodes made up in accordance with the invention, but without manganese, have a tendency to corrode at the solution surface line, and that this tendency is minimized by the addition of manganese to the alloy.

The addition of chromium or other chromium group metal to the electrode acts to harden the manganese oxide film or deposit on the anode. Thus, the manganese dioxide film is more resistant to abrasion in the case of cobalt-silicon-manganese anodes containing chromium than it is in the case of anodes of similar composition but without chromium, tungsten, molybdenum or uranium.

It will, therefore, be evident that while certain advantages of the invention are obtained without the inclusion of either manganese or a chromium group metal in the electrode that the presence of both of these materials is desirable, since the addition of these materials imparts to the anode further desirable properties. Thus, I have found that the addition of chromium to the anode greatly facilitates duplication of low loss, low voltage anodes. In other words, I can obtain and readily duplicate low loss, low voltage anodes more readily with chromium than without chromium.

The proportions hereinbefore mentioned of the various ingredients of my improved alloy generally represent what I now believe to be the preferred from of the invention. However, I wish it to be understood that these specific proportions mentioned may be somewhat varied without departing from the spirit of the invention. Thus, for example, I have found that by increasing the silicon content up to about 20%, I can bring the manganese content as high as 45%. This is of particular advantage in that it tends to lower the cost of the anode. In general, I may say that an anode embodying the principles of the invention in their complete

aspect should contain from about 7 to 20% silicon, from about 3 to 45% manganese, from about 4 to 10% chromium or the equivalent amount of tungsten, molybdenum or uranium and the balance cobalt, (including the aforementioned relatively small percentage of carbon).

In the production of the improved electrode of the present invention, I may employ cobalt with its normal impurities, including some small percentage of nickel, iron, manganese and carbon. I have obtained good results with cobalt containing around 4 to 7% of nickel and iron together therein. In the production of the anodes, I may proceed by melting the cobalt and adding charcoal thereto to increase its carbon content, or by simultaneously reducing a mixed oxide of cobalt, manganese and chromium, (or other chromium group metal). I may then add the silicon together with the manganese to the molten cobalt, but I have found that the addition of the silicon to the cobalt results in a violent evolution of heat, so that care should be taken to avoid the addition of such large amounts of silicon as will result in objectionable overheating. The silicon can be added gradually or as carbide of silicon or it may be combined with a small amount of cobalt and the resulting alloy or mixture added to the remaining portion of the cobalt. This violent evolution of heat which takes place when the silicon is added to cobalt is a further characteristic of the cobalt-silicon composition which distinguishes it from iron-silicon compositions.

The electrode of the present invention, in addition to its improved property of resisting anodic disintegration or corrosion, possesses in dilute sulfuric acid a relatively low anodic potential or voltage. In other words, the voltage between the anode and a copper cathode is relatively low, being approximately from about 1.8 to about 2.0 volts at 20° C. at an anode current density of about 20 amperes per square foot. This feature is of particular importance in the electrolytic production of copper, since it is instrumental in determining the terminal voltage which must be applied to the electrolyzing tanks or cells. The cost of electrolytically precipitating copper from an electrolyte is proportional to the voltage which must be applied, and from the standpoint of commercial economy, it is of the utmost importance that the surface tension voltage of the anode be as low as practicable. The cobalt-silicon electrode of the present invention, combining as it does a relatively low surface tension voltage with very effective resistance to anodic corrosion, makes a very durable, economical and satisfactory anode in the electrolytic precipitation of copper.

I claim:

1. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount and from 7 to 20 percent of silicon.

2. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount, from 7 to 20 percent of silicon and a depolarizing ingredient.

3. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount, manganese and from 7 to 20 percent of silicon.

4. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount, from 7 to 20 percent of silicon, a depolarizing ingredient and a hardening agent.

5. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount, manganese, chromium and from 7 to 20 percent of silicon.

6. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt, in predominant amount, manganese, chromium, from 7 to 20 percent of silicon and carbon.

7. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount, manganese, chromium and about 12 to 15 percent of silicon.

8. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount, 7 to 20 percent of silicon and 3 to 45 percent of manganese.

9. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount, 7 to 20 percent of silicon, 3 to 45 percent of manganese and 4 to 10 percent of chromium.

10. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount, 12 to 15 percent of silicon and 4 to 6 percent of manganese.

11. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount, 12 to 15 percent of silicon, and 4 to 6 percent of chromium.

12. An electrode resistant to anodic disintegration and made up of an alloy containing cobalt in predominant amount, 12 to 15 percent of silicon, 4 to 6 percent of manganese, and 4 to 6 percent of chromium.

13. An electrode resistant to anodic disintegration and having a low solution tension or voltage made up of an alloy of cobalt with about 12 to 15% of silicon, about 4 to 6% of manganese, about 4 to 6% of a chromium group metal and sufficient carbon to supply a small amount of graphitic carbon to the alloy.

14. An electrode resistant to anodic disintegration containing cobalt and silicon and structurally composed of two constituents, the first of which is relatively soluble in copper sulfate electrolytes and of good electrical conductivity and the second of which more or less envelopes the first and is relatively insoluble in copper sulfate electrolytes and of relatively low electrical conductivity.

15. An electrode resistant to anodic disintegration containing cobalt, silicon, manganese, and chromium and structurally composed of two constituents, the first of which is relatively soluble in copper sulfate electrolytes and of good electrical conductivity and the second of which more or less envelopes the first and is relatively insoluble in copper sulfate electrolytes and of relatively low electrical conductivity.

In testimony whereof I affix my signature.

COLIN G. FINK.