March 25, 1958 D. T. HURD 2,828,250

METHOD AND APPARATUS FOR THE ELECTROLYTIC OXIDATION OF COPPER WIRE

Filed June 28, 1955

Fig. 1.

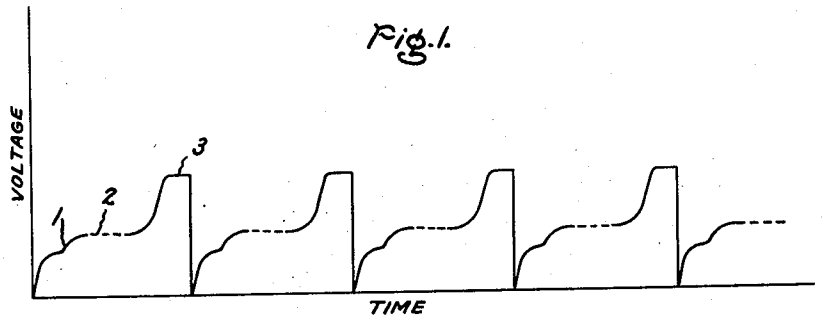
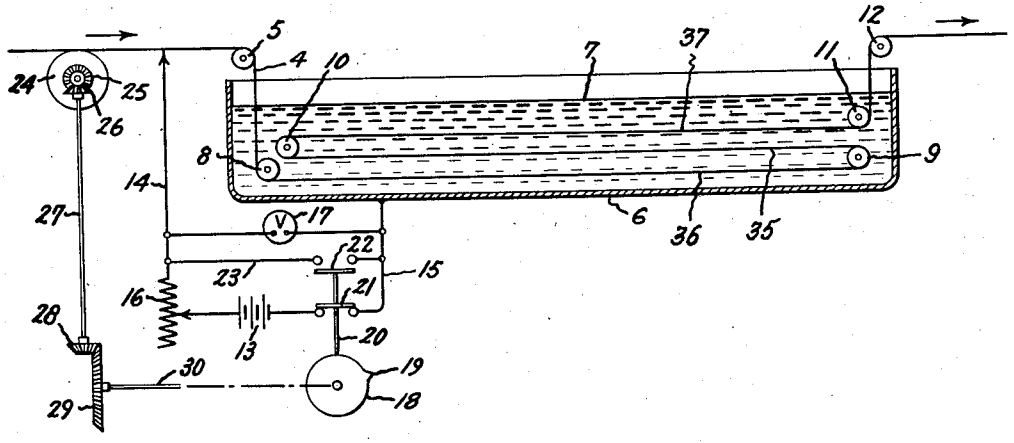


Fig. 2.



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United States Patent Office 2,828,250 Patented Mar. 25, 1958

2,828,250

METHOD AND APPARATUS FOR THE ELECTROLYTIC OXIDATION OF COPPER WIRE

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Application June 28, 1955, Serial No. 518,433

6 Claims. (Cl. 204—28)

The present invention relates to the formation of adherent films of black oxide on copper articles of extended length, such as, for example, copper wire. This application is a continuation-in-part of my application Serial No. 310,578, filed September 20, 1952, now abandoned, and assigned to the same assignee as the present application.

A layer of anodic black copper oxide on copper wire which has been prepared in accordance with my invention is a desirable substrate for resinous insulating materials applied on the wire in the fabrication of electrical conductors, such as, for example, magnet wire for use in the manufacture of motors, generators, transformers, and other electrical apparatus. The oxide film provides a firm bond for the adherence of the insulating coating, protects the coating from deterioration by chemical reaction with the metal of the conductor at elevated operating temperatures, retards attack of the conductor by atmospheric oxidation at elevated temperatures, and improves the abrasion-resistance of the insulation.

The development on copper articles of surface films of adherent black copper oxide by anodic electrolytic oxidation in a bath of hot concentrated caustic solution has been practiced heretofore as a batch process. Such surface oxidation by anodization heretofore has been carried out with articles of such limited size that the entire article could be immersed in a bath of chosen electrolyte. Thus, the entire immersed article could function as an anode to conduct current in cooperation with a suitable cathode and become superficially oxidized. The prior oxidation process practiced as a batch or static process is not well adapted for the oxidation of wires or similar objects of greatly extended length and especially not for continuous industrial production.

One of the known techniques for anodizing copper in a static bath of hot, aqueous, caustic solution provided with a suitable cathode comprises immersing the clean copper article in an electrolytic bath, connecting a unidirectional energy source voltage to the electrodes, making the article to be coated the anode in series with a suitable current limiting resistor, causing the electrolytic oxidation process to proceed until the current drops to a low level with or without the commencement of oxygen evolution at the anode which indicates termination of the anodization process, removing the article from the electrolyte, and washing and drying the article.

If one attempts to modify such process for the anodization of an extended length of copper wire by passing the wire continuously through an anodizing bath, one finds, surprisingly, after the withdrawal of the segment of wire which was in the bath at the start of operations and at the time of voltage application, that the wire following this segment emerges from the cell either without any apparent oxide film, or, at best, has only a very thin oxide film which is not at all suitable as a substratum for insulation, for which anodic copper oxide coatings of proper quality are uniquely desirable. Thus, even though an anodizing voltage is applied to the electrolytic cell, the anode wire passing through the cell remains passive and

does not become coated with a useful layer of black oxide.

Accordingly, it is an object of my invention to provide a rapid and continuous method of oxidizing extensive lengths of copper wire.

It is another object of the invention to provide an improved apparatus for the anodization of extensive lengths of copper wire.

Briefly stated, in accordance with one of its aspects, the present invention comprises an improved apparatus and process for anodizing extensive lengths of copper wire in which the wire is drawn continuously through an alkaline electrolyte to provide a coating of copper oxide thereon.

These and various other objects, features and advantages of the invention will be better understood from the following description taken in connection with the accompanying drawing in which:

Fig. 1 is a succession of graphs of anodizing voltage versus time for consecutive cycles in the anodization of an extended length of copper wire; and

Fig. 2 is a diagrammatic view of a preferred embodiment of my invention applied to an anodizing apparatus.

Fig. 1 discloses a succession of graphs of anodizing voltages plotted against time for consecutive cycles in the anodization of an extended length of copper wire. I have discovered that the voltage and the current in the anodizing process are important, and this is particularly true of the portion of the cell voltage which may be designated as the anode-to-electrolyte voltage. I have found that in order for the anodizing process to proceed it is necessary that the passivity of the copper be destroyed, and in order to do this the electrolytic process should start at or below a certain minimum anode-to-electrolyte voltage. The value of this critical anode-to-electrolyte voltage, which is measured with a mercury-mercury oxide probe electrode in the solution, is under the usual electrolytic conditions about +0.2 volt. The anode remains passive for extended periods if this voltage is exceeded when unoxidized copper is drawn into the electrolyte. The value of the initial overall or cell voltage corresponding to this anode voltage in any given instance will depend on a number of variables, including the nature of the cathode and its previous history, the composition and temperature of the electrolytic solution, the current density, and the polarization, if any, of the cathode. Thus, the minimum value of overall cell voltage is from about 0.4 volt to higher voltages depending on the above-mentioned variables, and in some cases may be as high as about 0.9 volt. At such initial cell voltages, with the anode-to-electrolyte voltage rising from at or below about +0.2 volt, it is possible in an anodization process to build up continuous coatings of black copper oxide comprising a mixture of cuprous and cupric oxides of relatively substantial thickness. In some cases, coatings as thick as several tenths of a mil have been produced on the surface of a copper wire anode. In this range of operating conditions, the coating thickness and the time required for completion of the anodization process are roughly proportional to the inverse of the anode current density.

In an anodization process with a fixed voltage source and series resistor which is more fully explained hereinbelow in the discussion of Fig. 2, the cell voltage and anode current density vary with time during the anodizations process as illustrated by any one unit graph of Fig. 1. Initially, the cell voltage rises at the beginning of each anodizing cycle as indicated at 1 from a cell voltage below about 0.4 volt with an anode-to-electrolyte voltage below about 0.2 volt to an intermediate value at 2 which is shown by a broken line of variable length. At this intermediate stage a voltage of about 0.9 to 1.3 volts builds up the oxide film. The anodization process over most of the cycle is one of substantially constant voltage as indicated by the broken line. As the coating reaches its desired thickness,

the cycle is characterized by a rapid increase in electrical resistance of the coating, providing in effect a self-limiting process, and the cell voltage rises to a value of from 1.5 volts to 2.0 volts near the end of the cycle at 3, which rise is valuable to seal and to render less porous the anodic coating. The cell voltage finally is caused to fall again to below 0.4 volt, as will be more fully explained hereinbelow, to initiate coating on the fresh, unanodized portion of wire drawn into the bath during the previous cycle. As the cell voltage and the anode current density are related variables, the current has not been shown. Since the resistance of the cell changes with time and the course of the anodization process, the current falls as the voltage rises at the end of the anodizing cycle.

If the cell voltage is maintained at a very narrow level, normally between 0.9 and 1.2 volts, for example, by being derived from an adjustable voltage source of very low internal resistance (that is, having an internal resistance which is negligible in comparison with the resistance changes that occur in the cell during the anodization process because of the build-up of oxide coating on the anode, polarization of the electrodes, etc.), I have found that in this voltage range a black anodic coating may be obtained on the anode at a maintained constant voltage corresponding to the intermediate broken line plateau on the voltage-versus-time graph of Fig. 1, but without the initial and final periods of rising voltage illustrated in this figure. Thus, under such special conditions of very close control of voltage and current, it is possible to obtain a black oxide coating on copper wire which is continuously passing through the electrolytic bath. The voltage and current must be supplied at values determined by the residence time of a particular segment or incremental length of wire in the bath.

However, such a process has serious disadvantages for the continuous anodic oxidation of extended lengths of copper wire as compared with the improved method herein described and claimed. While the present process requires a close control of the overall cell voltage, an important voltage in the anodization process is the anode-to-electrolyte voltage. If the cathode-to-electrolyte voltage should change for any reason during the continuous operation of the process as described above, the anodization conditions may so change that the quality of the coating is deteriorated or the anodization process may be interrupted entirely. Ordinarily, should a copper wire enter an electrolytic bath under the usual conditions of anodization, while a segment already in the bath is undergoing the latter stages of the anodization process, such entering wire will remain passive and unoxidized.

In Fig. 2 of the drawing, a wire **4** which is of any desired diameter is paid out from a source (not shown) and passes over a guide **5** into a container **6** with an electrolyte **7** therein. Container **6** is fabricated in any desired size of conductive material such as, for example, iron or copper which is not attacked by electrolyte **7**. However, the length of wire **4** within container **6** is increased by traversing such wire in a back and forth path over guides **8**, **9**, **10** and **11** which are mounted in container **6** under the surface of electrolyte **7**. Wire **4** passes from electrolyte **7** over a guide **12** adjacent container **6** to be washed and dried by suitable apparatus (not shown). The anodized wire may be coated as described in my copending application, Serial No. 310,577, filed September 20, 1952, and assigned to the same assignee as the present application.

The electrical circuit for the anodizing apparatus comprises a D. C. power source, such as, for example, a primary 2 volt battery **13** which is connected by a pair of conductors **14** and **15** to wire **4** as anode and to container **6** as cathode. A variable resistor **16** is provided in the circuit between battery **13** and conductor **14** to adjust the initial cell voltage to a value which produces the voltage versus time graph in Fig. 1 for a particular wire speed. A voltmeter **17** is connected across conductors **14** and **15** to indicate the voltage between wire **4** and container **6**. I provide further a mechanism for momentarily short-circuiting the anode to the cathode circuit which comprises a cam **18** with a protuberance **19** to act against a shaft **20** with a pair of spaced switches **21** and **22** thereon. Switch **21** opens and closes the circuit through conductors **14** and **15** while switch **22** acts in a similar manner in a circuit **23** across conductors **14** and **15**. While the anode to cathode circuit may be short-circuited manually by rotating protuberance **19** of cam **18** to move shaft **20** whereby the anode to cathode circuit is opened and circuit **23** is closed, cam **18** is shown to be rotated automatically in response to the speed of wire **4** through a suitable gear arrangement.

Cam **18** is automatically rotated in a time relationship with the speed of wire **4**. Wire **4** is drawn into container **6** over a guide **24** which guide **24** is rotated at any desired speed by a power source, such as, for example, a motor (not shown). Bevel gear **25** drives a bevel gear **26** to rotate a shaft **27** which carries a bevel gear **28** at its opposite end. Gear **28** meshes with a bevel gear **29** of wider diameter on a shaft **30**. Cam **18** with a bevel gear (not shown) is rotated by a similar bevel gear (not shown) on the opposite end of shaft **30**.

Electrolyte **7** in electrolytic container **6** is ordinarily an aqueous sodium hydroxide solution, although certain other strong alkali metal bases may be used, for example, potassium hydroxide. The electrolyte concentration of NaOH or KOH is ordinarily chosen from about 13 to 40 percent by weight of alkali, 15 to 20 percent being a preferred range of composition but the concentration is not critical and a higher or lower concentration may be used. The operating temperature should be from about 85° C. to 105° C., and preferably 95° C. to 98° C.

In the operation of my apparatus for anodizing copper wire which is disclosed in Fig. 2, wire **4** of any desired diameter is passed over guides **24**, **5**, **8**, **9**, **10**, **11** and **12** to traverse electrolyte **7** in container **6** at any suitable wire speed. A time interval, such as, for example, 60 seconds is selected for the anodization cycle of the wire segment in electrolyte **7**. The ratio of the number of revolutions of guide **24** to a single revolution of cam **18** in a 60 second cycle is set, such as, for example, by an appropriate size bevel gear **29** on shaft **30**. Thus, the anode to cathode voltage will be short-circuited every 60 second period. Resistor **16** is varied during wire travel through electrolyte **7** until a voltage profile is established as set forth in Fig. 1. Such voltage profile is checked by voltmeter **17** which is connected across conductors **14** and **15**. When the voltage profile of Fig. 1 is established, the anodization process proceeds continuously. Wire **4** is examined to determine if the copper oxide coating is of sufficient thickness for its intended use. The above procedure may be repeated with a different wire speed and time cycle to provide a different coating thickness.

I have found that it is not sufficient merely to remove the applied voltage at the end of each coating cycle. The electrolytic action of the already anodized wire in the bath maintains the cell voltage to such an extent that, without a momentary short-circuiting of the anode to the cathode, the voltage is not lowered rapidly enough below the initial cell voltage with an anode-to-electrolyte voltage of about 0.2 volt to destroy the passivity of, and commence an immediate subsequent anodization cycle of, the next adjacent segment of wire within the electrolyte. A first switch **21** disconnects the applied voltage while a second switch **22** short-circuits the anode to the cathode momentarily to provide the necessary drop in voltage which is accomplished in a brief time interval of one-half to one-quarter second. Thus, cam **18** is timed to open switch **21** and close switch **22** at intervals which correspond to the rate of travel of wire **4** to cause anodization to occur in unbroken continuity.

Other suitable automatic means could be provided

within the compass of my invention for short-circuiting the anode to cathode circuit, such as, for example, a timer and actuating mechanism (not shown) to rotate cam 18 in response to the predetermined rate of wire travel or an electronic control (not shown) to sense the voltage changes in the course of the anodization cycle and to actuate momentarily a shunting mechanism between conductors 14 and 15 at point 3 on the anodization cycle. Since the time required for the completion of the anodizing process for the particular section of wire being anodized at any one time in the bath can be adjusted by means of the voltage of the source 13 and the series current-limiting resistor 16, the cycle can be adjusted to match the residence time of the wire in the bath which, in turn, depends on the length of the electrolyte bath and the speed or rate at which the wire is passing through it. If it is desired to subject the anode wire to a longer residence time in the bath without an increase in the container size the wire may be caused to traverse a multiple path back-and-forth on a plurality of guides 8 to 11 within electrolyte 7, as indicated in Fig. 2.

In Fig. 2, a segment 35 of wire 4 which is being anodized at a specific wire speed must remain in electrolyte 7 of container 6 during one complete voltage cycle as shown in a unit graph in Fig. 1. It is necessary that an additional segment 36 of wire 4 enter the electrolytic bath during the anodization of segment 35 to provide a continuous process. However, segment 36 of wire 4 which enters electrolyte 7 after the commencement of the anodization cycle of segment 35 remains essentially passive until the next short-circuiting of the anode to the cathode circuit. A segment 37 of wire 4 which was anodized during a previous cycle is shown emerging from container 6 during anodization of segment 35. Such segment 37 is not affected by the oxidation of segment 35. Thus, the length of wire 4 within electrolyte 7 must be at least about twice the length of the segment which is being oxidized during a specific voltage cycle or pulse to cause anodization in unbroken continuity.

With an automatic device to control the cycle of the process, a close degree of control can be exercised through small adjustments of the series resistor 16 to correct for minor changes in operating variables, such as changes in the temperature of the electrolyte. By automatic coordination in a process such as I have described, the anodization process can be utilized for the continuous anodization of extended lengths of copper wire of varying sizes and with the production of anodic coats of various desired thicknesses.

Example 1

The following specific example is given as an illustration and not as a limitation of my invention. An anodizing apparatus which was similar to Fig. 2 was provided with a five foot electrolyte container with a single wire path. A solution of 16% by weight of sodium hydroxide at a temperature of 95° C. was provided for the container. A 1½ volt battery and 1/10 ohm resistance in the circuit provided a voltage profile similar to Fig. 1. Fifty mil diameter copper wire was passed through the electrolyte in the container at the rate of 5 feet per minute. The anodization cycle was of 10 second duration in which the voltage was dropped below an initial cell voltage of 0.4 volt with an anode-to-electrolyte voltage of 0.2 volt between successive voltage pulses or cycles. A continuously good thin coating of black copper oxide was produced on the wire.

Example 2

An anodizing apparatus which was similar to Fig. 2 was provided with a five foot container with a multiple wire path. The container was filled with a solution of 18% by weight of sodium hydroxide at a temperature of 98°C. The electrical circuit employed a 2 volt battery and a resistor with a 1/10 ohm resistance to provide a voltage profile as shown in Fig. 1. Copper wire of a 50 mil diameter was passed through the electrolyte in the container at 4 feet per minute. A 40 second anodization cycle was used with momentary interruption of the voltage between each such cycle to drop the voltage to the initial value in Example 1. The wire which emerged from the container had a good black coating of copper oxide thereon.

Example 3

An anodizing apparatus was employed which was similar to Example 2. A five foot electrolyte container was provided with a solution of 20% by weight of sodium hydroxide at a temperature of 93° C. Copper wire of a 32 mil diameter was passed through the electrolyte at the rate of 8 feet per minute. The electrical circuit included a 2 volt battery and a resistor with 5/10 ohm resistance. A 20 second anodization cycle produced wire with a good black copper oxide coating. The voltage was interrupted between cycles as set forth in Example 1.

As will be apparent to those skilled in the art, the objects of my invention are attained by drawing a copper wire through an alkaline electrolyte in which a voltage cycle is short-circuited at spaced intervals to provide a coating of copper oxide on the wire.

While other modifications of this invention and variations of apparatus which may be employed within the scope of the invention have not been described, the invention is intended to include all such as may be embraced within the following claims.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of oxidizing copper wire which comprises causing said wire to travel through an electrolytic cell having a cathode and an aqueous alkaline electrolyte which is capable of producing anodic oxidation, subjecting said wire as anode during such travel to successive pulses of unidirectional voltage, the voltage during each pulse passing from a low value at which oxidation will be initiated to a higher value at which oxidation will be augmented, providing a momentary short-circuiting of said anode and said cathode between said successive pulses, and so timing the starting and duration of said pulses with respect to the rate of travel of said wire that consecutive lengths of wire are oxidized in unbroken continuity.

2. The method of carrying out anodic oxidation of copper wire of extensive length in an electrolytic bath having a cathode and an aqueous solution of a strong alkali which comprises passing said wire in continuous travel through the alkaline solution of said electrolytic bath, during said travel subjecting said wire as anode to successive pulses of unidirectional voltage, the voltage of said pulses rising from about below 0.4 volt to about 2 volts for respectively starting and augmenting oxidation, providing a momentary short-circuiting of said anode and said cathode between said successive pulses, and coordinating the speed of wire travel with the length and spacing of said pulses to cause an unbroken film of oxide to be produced on said wire.

3. The method of continuously oxidizing an extended length of copper wire which comprises continuously feeding said wire as anode through an electrolytic cell having a cathode and an aqueous alkaline electrolyte, subjecting a segment of said wire during passage within said cell to a pulse of unidirectional voltage, the voltage during said pulse passing from a low value at which oxidation will be initiated to a higher value at which oxidation will be augmented, providing a momentary short-circuiting of said anode and said cathode at the end of said pulse, said feeding providing a successive segment of said wire in said cell during the subjection of said first segment to the voltage pulse whereby the portion of wire within said cell is at least twice the length

of the wire segment being anodized, and repeating said voltage pulse and short-circuiting for each successive wire segment after said first segment to produce an unbroken film of oxide on said wire.

4. In an apparatus for producing a film of oxide on copper containing wire of extensive length including an electrolytic cell having a cathode and an aqueous alkaline electrolyte therein, the combination comprising means for causing the wire to be oxidized to travel through said cell in contact with said electrolyte, a source of voltage connected to said wire and said cathode, means for conducting between lengths of said wire functioning as anode and the cathode of said cell successive pulses of unidirectional voltage having an initial voltage adapted to start anodic oxidation and a succeeding higher voltage adapted to augment oxidation, and circuit interruption means for momentarily short-circuiting said anode and said cathode between said successive pulses, and means connecting said circuit interrupting means to said drive means for timing said pulses of voltage with the travel of said wire to cause successive lengths of oxide coatings to follow in unbroken continuity on said wire.

5. In an apparatus for producing a film of oxide on copper containing wire of extensive length including an electrolytic cell having a cathode and an aqueous alkaline electrolyte therein, the combination comprising guide means for causing wire to be oxidized to travel through said cell in contact with said electrolyte, a source of voltage connected to said wire and said cathode, electrical switching means for impressing between lengths of said wire functioning as anode and the cathode of said cell successive voltage pulses having an initial voltage adapted to start anodic oxidation and a succeeding higher voltage adapted to augment oxidation, said switching means including a first switch, means for momentarily short-circuiting said anode and said cathode between said successive pulses, and a second switch for interrupting and restoring anodizing current flow and a cam driven by said guide means to operate said switches in response to a predetermined rate of travel of said wire whereby successive lengths of wire are oxidized in unbroken succession.

6. In an apparatus for producing a film of oxide on copper containing wire of extensive length including an electrolytic cell having a cathode and an aqueous alkaline electrolyte therein, the combination comprising a guide for causing wire to be oxidized to travel through said cell in contact with said electrolyte, a source of voltage connected to said wire and said cathode, electrical switching means for impressing between lengths of said wire functioning as anode and the cathode of said cell successive voltage pulses having an initial voltage adapted to start anodic oxidation and a succeeding higher voltage adapted to augment oxidation, said means for impressing including a first switch to momentarily short-circuit said anode to said cathode between said successive pulses, a second switch for interrupting and restoring anodizing current flow, a rotary cam driven by said guide means and arranged to simultaneously operate said switches whereby said switches are responsive to a predetermined rate of travel of said wire and successive lengths of wire are oxidized in unbroken succession.

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