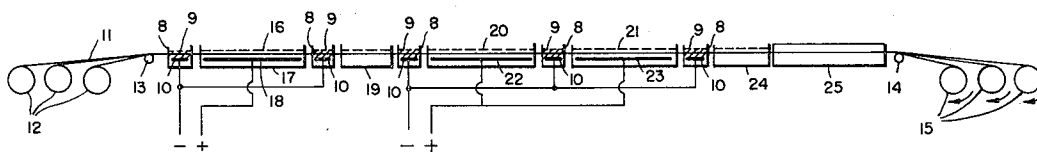
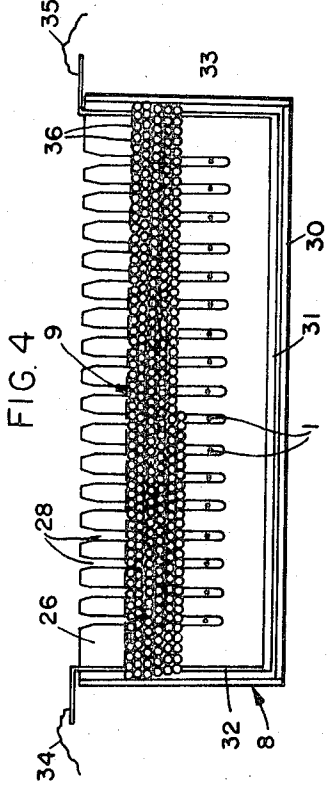
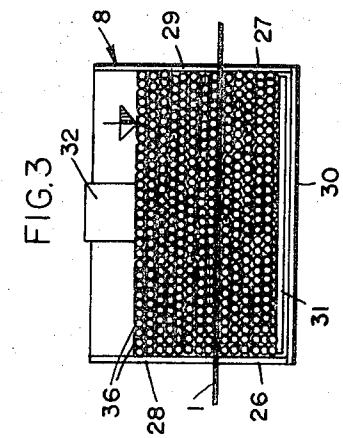
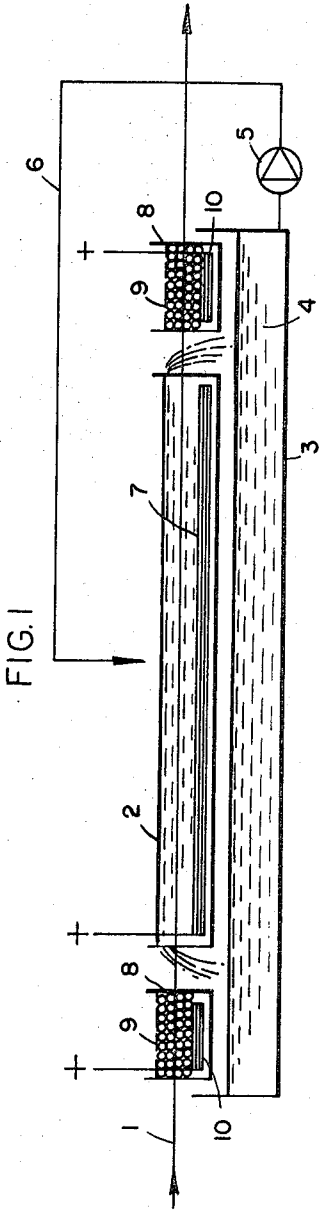
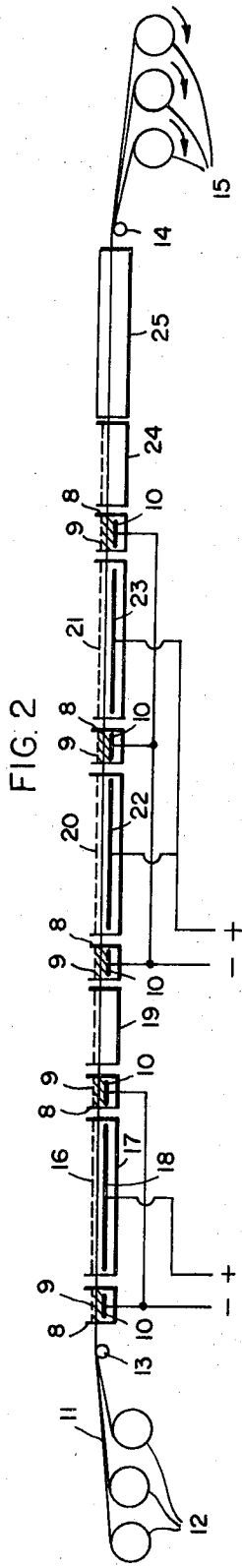


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PROCESS AND APPARATUS FOR ELECTROLYTIC TREATMENT OF TRANSPORTED WIRES

A number of techniques are known for the purpose of providing an electrical contact of wires which are being conducted through an electrolytic bath, e.g., in apparatus for etching, galvanizing, plating, or otherwise electrolytically treating the wires. For example, movable metallic rolls can be used for supplying current to the transported wires, the current supply to the rolls occurring over a common fixed axis and the rolls being driven by winding or looping the wires around their circumference. This arrangement is unsatisfactory because the metallic rolls are rather quickly worn away, both on their inner contact surfaces where they journaled on the fixed axis and also on their outer facing surfaces in contact with the transported wires, such wear being caused by the braking and notching effects caused by the relatively rapidly transported wires. Also, since these metallic rolls are susceptible to corrosion, e.g., as caused by the electrolytic bath and especially etching or pickling baths, a gradual corrosion accelerates the mechanically influenced wear or deterioration of the fixed axis, the bushing of the rolls and also the wire-contacting surface of the rolls which are often grooved. Therefore, when using such rolls for an electrical contact with the running wires, frequent repairs or replacement of many parts cannot be avoided.

The supply of current to the wires can also be accomplished by using a metal drum or cylinder over which the wires are likewise carried with at least some degree of winding, an electrical contact with the metal drum taking place by means of conventional carbon brushes. Such a metallic drum is likewise subject to a considerably large and rapid mechanical wear because it is generally impossible to draw many wires over this metallic drum at exactly the same speed. Where the drum is rotatably driven by the wires, it necessarily assumes an average circumferential velocity so that individual wires running slightly slower or faster than this velocity cut into the circumferential surface over a period of time.

In another technique, each individual wire being transported through the electrolytic bath is maintained in electrical contact by being slightly twisted around and in running contact with individual fixed, current-conducting wires so that current is supplied directly from the fixed wires to the running wires. Again, however, the cutting effect of the running wires causes a very rapid wear of the fixed contact wires so that continuous supervision and inspection is necessary for frequent replacement of the fixed wires. Moreover, this current-conducting technique requires a relatively large clearance between the individual wires when treating a large number of running wires, and this substantially reduces the capacity of the operation.

One object of the present invention is to provide an improved method or means for supplying current to a plurality of wires as they are conducted an electrolytic bath in any conventional electrolytic treatment. In particular, it is an object of the invention to provide electrical contacting means for the running wires in such a manner as to avoid constant supervision and frequent replacement of the contacting or current-supplying elements. Other objects and advantages of the invention will become more apparent upon reconsideration of the following detailed disclosure.

It has now been found, in accordance with the invention, that a substantial improvement can be achieved in a process for the electrolytic treatment of a plurality of wires being transported through an electrolytic bath by guiding the wires to be treated in running contact with a granular conductor of the first class arranged in at least one layered zone or bed externally of the bath. The granular conductor of the first class is advantageously arranged as a layer in a nonconducting container so as to surround the transported path of the wires for electrical contact therewith, i.e., such that the granular conductor is located both above and below the path of the wires. An electrode can be inserted at the bottom portion of the nonconducting container to supply current to the entire layer of the granular conductor. Also, it is preferable to arrange a non-

conducting container for the granular material at both ends of each electrolytic bath in which the running wires are treated. In other respects, relatively conventional apparatus can be employed including an electrolytic bath means for the electrolyte including a current-supply electrode, and also means to transport the wires through the bath or electrolyte and the nonconducting container which can be slotted in its oppositely facing sidewalls for passage of the wires therethrough.

The expression "conductor of the first class" is employed herein in view of the well-known sharp division of electrical conductors into three classes. The first class of conductors, sometimes referred to as metallic or electronic conductors, consists of the metals, alloys and a few other substances such as carbon. By comparison, conductors of the second class are electrolyte conductors, while third class conductors are mixed conductors wherein current passes partly in a metallic and partly in an electrolytic manner. The granular conductors of the present invention are restricted to first class conductors consisting essentially of a highly electrically conductive solid material. For example, one can select metals such as copper, nickel or aluminum or alloys such as Monel, Hastelloy, brass or steels. Electrical carbon or graphite may also be employed as the granular conductor. As is known, the choice of such a conductor will depend to some extent upon the manner in which the running wires are being treated, i.e., whether they must act as the anode or the cathode in the electrolytic bath. The choice of the most suitable granular material to provide electrical contact with the wires may also be determined by the desirability of employing a corrosion-resistant material as well as one which will properly handle the current supply. In this respect, the selection of any particular granular conductor of the first class can be easily made by one skilled in this art, based upon the normal conditions placed upon such conducting materials by any particular electrolytic process. It has been found to be particularly advantageous to supply the layer or bed of the nonconducting container with particles of the first class conductor which have a substantially uniform cubical or spherical shape.

The invention is further explained in connection with the accompanying drawings in which:

FIG. 1 is a partially schematic cross-sectional view taken longitudinally through a typical electrolytic bath which has been equipped in accordance with the invention.

FIG. 2 is a schematic illustration of an overall process for the electrolytic treatment of a plurality of wires as they are conducted through several treatment baths of zones.

FIG. 3 is a vertical cross-sectional view of one embodiment of a nonconducting container which holds a layer of the granular first class conductor, the cross section being taken in the longitudinal or running direction of the planar group of wires being treated; and

FIG. 4 is a vertical cross-sectional view of the same nonconducting container taken transversely to the longitudinal or running direction of the planar group of wires.

Referring first to FIG. 1, a planar group of wires 1 are conducted in the direction of the arrows through an electrolytic cell or treatment bath 2 which is supported by any suitable means above and slightly within a primary vessel 3 for the bath liquid 4. This bath liquid is circulated from the lower vessel or tank 3 by means of pump 5 through fluid conduit 6 into the electrolytic cell 2 where excess bath liquid overflows at either end. This cell 2 is equipped with an anodic electrode 7, in accordance with any conventional construction for an electrolytic cell, and the planar group of wires 1 are conducted through the cell 2 at a predetermined distance from the anode 7. At either end of the electrolytic cell 2, a nonconducting container 8 is mounted in any suitable manner and holds a layer or bed 9 of a granular first class conductor with suitable means such as slotted walls for transporting the planar group of wires 1 through each bed 9 as well as through the electrolytic cell 2. Each container 8 is also provided with a suitable electrode 10, in this instance a cathode, which is preferably located at the bottom of the container. These individual non-

conducting containers 8 and the function of the granular conductor 9 is explained in greater detail in connection with FIGS. 3 and 4.

A typical overall process is illustrated in FIG. 2 in which a plurality of wires 11 are drawn from the feed rolls 12, if desired with suitable braking means such as a friction brake on the rolls 12, and the individual wires are then collected into a horizontal planar group over the guide roller 13 or similar guide means so as to be conducted through a series of treatment baths or zones and finally taken off over a second guide means 14 onto individual takeup spools or cylinders 15. It is of course important that the planar group of wires be drawn through the entire system by the takeup rolls 15 under sufficient tension so as to be properly situated or located in each of the treatment baths or zones.

In this typical embodiment of an overall process as shown in FIG. 2, the wires 11 can be first conducted through a pickling or etching bath 16 contained within the cell 17 having an anode 18. The wires 11 can then run through a water bath 19 into a number of sequentially arranged electrolytic cells 20 and 21 containing anodes 22 and 23, respectively, e.g., in order to plate the wires with brass, zinc or some other typical plating material. Finally, the wires 11 are transported through a second water bath 24 and a drying chamber 25 and then collected in a conventional manner. Individual nonconducting containers 8 for the granular first class conductor material 9 are arranged at each end of the electrolytic cells 16, 20 and 21 in order to provide a cathodic connection at 10, e.g., as shown on a somewhat larger scale for an individual electrolytic cell in FIG. 1. The primary vessel or tank 3 as well as the recirculation of the electrolytic bath fluid has been omitted from FIG. 2 in order to simplify the schematic flowsheet as much as possible.

An especially preferred embodiment of the nonconducting container of the invention with its layer or bed of a granular first class conductor is illustrated in detail in FIGS. 3 and 4 by showing a longitudinal and transverse cross section, respectively, with reference to the running direction of the planar group of wires 8 being transported therethrough.

The opposing vertical sidewalls 26 and 27 of the nonconducting container 8 are arranged transversely and preferably perpendicularly to the horizontally transported planar group of wires 1 and are provided with vertical slots 28 and 29 for the entry and exit of the wires as they pass through the container. On or near the floor 30 of the container 8, there is located an electrode 31 connected to a suitable source of electrical current supply through vertically mounted connecting rods or bars 32 and 33 at either or both ends of container 8. The electrode 31 can have any conventional structure with appropriate connection to a current supply line or lines 34 and 35. This electrode may be either positive or negative depending upon the polarity to be exhibited by the transported wires.

The first class granular conductor 9 is arranged above and below the planar group of wires 1 and causes current to flow between the electrode 31 and these wires. In this instance, the granular conductor is made up of individual spherical particles 36 which are preferably uniform in size as supplied to the container in arranging a bed or layer around the wires.

The vertical slots 28 and 29 in the oppositely facing sidewalls of the container 8 may be sufficiently large to permit the use of different wire sizes, e.g., with a slot width of about 2-4 mm. It is especially desirable to arrange these slots at uniform intervals so that the individual running wires are carried substantially parallel to one another at approximately equal intervals. The container itself can be constructed of any suitable nonconducting material including various plastics and preferably fiber-reinforced plastics such as polyvinyl chloride, polycarbonates, melamine resins and the like. In order to avoid wear or damage to the container by occasional contact with the running wires, the laterally exposed surfaces of the slots 28 and 29 can be protected by inserting pins or other such suitable liners of a hard and wear-resistant material such as a sintered aluminum oxide supplemented by various metal

carbides. The slots are then fully adapted to function as guides for the transported wires.

The size and shape of the particles or granules of the first class conductor material which provides the electrically conducting bed can vary within a relatively broad range. It is important, however, that the individual granules be sufficiently large to prevent their withdrawal or ejection through the slots in the container. On the other hand, these granules must not be so large as to cause the individual wires to deviate substantially from their linear and preferably parallel path through the container. In other words, the individual wires should be capable of clearing a relatively straight path through the container without being turned laterally toward one side or the other. The height of the granular bed above the planar group of wires is also limited to some extent for this same reason, i.e., to prevent a vertical bending or deflection in the path of the wires as well as a lateral or horizontal deflection. These criteria can be readily determined by a few preliminary experiments with any suitable granular first class conductor having various sizes or shapes.

By way of example, it has been found especially favorable in the electrolytic deposition of brass onto steel wire with a diameter of 0.8 mm. to employ a granular conductor composed of cubical brass cuttings whose sides have a length of 4 mm. In this particular process, however, successful results have also been achieved with cubical brass cuttings having a side length of 8 mm. or with spherical brass granules having a similar diameters.

In general, then, with slots having a width of about 2-4 mm. and using wire sizes of about 0.6-1.5 mm. in diameter, the size or diameter of the contact material or granular first class conductor should preferably be at least about 1 mm. larger than the slot width up to a maximum size of about 10-12 mm. At the same time, the individual parallel wires are preferably spaced at an interval which is substantially larger than the size or diameter of the contacting granules, e.g., 1 and ½ to two times the diameter of the granules or even more. With the above-noted dimensions for the wires, slots and granules, one can thus space the wires at intervals of up to approximately 25 mm. It is desirable to space the wires as closely as possible in order to achieve a maximum capacity of a single-operating unit while also using the smallest possible electrolytic bath.

When treating very fine wires or unusually large diameter wires, it will be recognized that suitable adjustments must be made in the various dimensions so that the above information applies with reference to a somewhat limited or special case. It is an advantage of the invention that a single-slotted container with an intermediate particle size of the granular conductor can be used to supply current to varying sizes of wires so that the same unit can be used in many different operations.

In carrying out the process of the invention, it has been found to be especially advantageous to transport the wires through the nonconducting container at a substantial distance below the upper surface of the layered zone or bed of the granular first class conductor. In particular, it has been found most useful to position about two-thirds to four-fifths of the layer of the granular conductor above the transported path of the wires through the container. In other words, the planar group of wires 1 preferably divides the height of the layer into proportions or lower and upper layers of 1:2 to 1:5, as measured upwardly from the electrode located in bottom portion of the container. The contact pressure of the granular conductor located above the running wires with this arrangement tends to favor a good conduction of the current to the wires. At the same time, however, good conduction of current from the electrode to the wires is also favored by maintaining a large number of contact points between each wire and the surrounding granules, e.g., by employing sufficiently small granules as well as selecting an appropriate shape of the granules. The degree of contact with the wires in either a stationary or running condition can be readily determined by electrical measurements to ensure proper operation of the device before it is placed in operation for continuous industrial processes.

The running wires cause a partial intermixing of the granular conductor, and although there occurs a partial wearing or reduction in size of the granules, fresh granulated material can be introduced during the transport of the wires by adding the granules to the top of the bed. Since electrolytic processes are generally stopped for cleaning periodically, e.g., every 1-2 weeks, excessively small particles can be sorted out at such intervals to avoid too great a loss of granular material through the container slots.

The invention is further illustrated but not limited by the following examples.

EXAMPLE 1

Electrolytic Etching.

In order to demonstrate one embodiment of the invention for providing satisfactory electrical contact and current supply in an electrolytic etching process, a planar group of steel wires to be patinated or etched is selected so as to provide 32 individual wires with a diameter of 0.8 mm. for each wire. The etching or patination of the wires takes place under conventional conditions at 900° C. and the wires are then quenched in a lead bath at about 520° C.

The steel wires are drawn at a linear velocity of 40 meters/minute through two nonconducting containers 8 as shown in FIGS. 3 and 4 positioned at each end of the etching bath as generally illustrated in FIGS. 1 and 2. The first container is located about 20 cm. before the etching bath while the second container is located the same distance after the bath, i.e., in the running direction of the wires. Each container 8 is filled with a cubical granulate having side dimensions of 4 mm. to provide a bed or layer height of 80 mm. The cubical granulate is composed of Hastelloy C which is an alloy of approximately the following composition: 51% Ni, 15.5-17.5% Cr, 16-18% Mo, 4-5% W, 4-7% Fe and 0.15% C. The length of the nonconducting container amounts to 25 cm., and its breadth (transverse to the running wires) amounts to 90 cm. The planar group of wires runs horizontally through vertical slots having a width of approximately 2 mm. so that the wires are spaced parallel to one another at an interval of about 25 mm. The planar group of wires is positioned within the granular bed at a height of about 20 mm. from the cathode, i.e., the electrode located at the bottom of the container, so that about three-fourths of the granular bed lies above the planar group of wires. The cathode is a carbon electrode.

The etching bath is 2.60 meters long and is equipped with a conventional carbon anode. The electrolyte of the bath is a 15 percent hydrochloric acid. A current of 15 amperes is applied to each individual wire, which corresponds to a voltage or potential of approximately 7 volts, taking into consideration the length of the bath and the electrical resistance. The group of wires leaves the etching bath in a white etched condition which is thus uniformly freed of the dark gray oxide layer.

Similar good etching results have been achieved under substantially the same test conditions as the foregoing example by using each of the following granulated conductors:

- a. Hastelloy A (an alloy of 53% Ni, 22% Fe, 22% Mo, 1% Si and 2% Mn);
- b. Hastelloy B (an alloy of about 61% Ni, 26-30% Mo, 4-7% Fe and 0.12% C);
- c. Hastelloy D (an alloy of about 83% Ni, 2% Fe, 7.5-8.5% Si and 0.12% C);
- d. Monel; and
- e. Electrical graphite.

EXAMPLE 2

Electrolytic Plating.

The etched and then thoroughly washed steel wires after being etched as in Example 1 are electrolytically plated with brass. The simultaneous deposition of copper and brass take place in the usual manner in an alkaline cyanide solution with the use of a Cu/Zn-anode (having a copper:zinc ratio of 70:30).

The wires are drawn through the plating bath as shown in FIG. 1 at a linear velocity of 40 meters/minute, with the nonconducting containers located before and after the bath in the same manner as in Example 1. In each case, the container is filled to a layer height of 60 mm. with prismatic or columnar granules having a thickness of 5 mm. and a height of 6 mm. The planar group of wires passes through the granular bed at a distance of 20 mm. from the cathode at the bottom of the container, the cathode in this instance being a V4A-electrode.

A current of 15 amperes is applied to each individual wire, corresponding to a potential of 6.9 volts when considering a plating bath length of 2.80 meters and the electrical resistance. The wires leave the plating bath with a uniform brass coating of 0.4 microns.

From the above examples, it will be recognized that the present invention offers a highly satisfactory technique for conducting a large number of wires continuously through two or even several electrolytic baths, e.g., as in sequential etching and plating operations. Also, the method and apparatus of the invention are widely applicable to any electrolytic treatment of steel, iron or other metallic wires which requires a consistent and uniform supply of electrical current to the wires. For example, in addition to an acid etching where an outer oxide scale or layer is effectively removed in spite of the strong development of gas at the electrodes during electrolytic decomposition, other preliminary treatments of the wires are also equally successful as in scouring or degreasing by electrolytic means. Also, in addition to all types of electrolytic plating processes, the invention is also useful in finishing treatments such as electrolytic polishing which generally requires an anodic decomposition of the material being polished. It is thus immaterial whether the electrolytic reaction taking place on the transported wires is to be carried out anodically or cathodically.

The granular first class conductor material employed in accordance with the invention exhibits a considerably smaller mechanical tension on the transported wires as compared to relatively massive rotating rollers or so-called contact drums or cylinders. While the use of the latter of these mechanically tensioning and contacting means often raises the tension to the breaking point limits, especially with thinner wires, this effect does not occur with the technique of the present invention and there are considerably fewer disturbances or work stoppages from the breaking of individual wires. Also, there is much less need to interrupt the running of the wires in order to replace current supplying elements even though there is an eventual mechanical wear or corrosive decomposition of the granular first class conductor. If desired, means can be provided to slowly removed granular material from the bottom portion of the nonconducting container while adding fresh granules at the top. Such modifications can be easily accomplished within the scope of the invention.

Naturally, in view of this more effective operation, the electrical contacting means of the invention including the nonconducting container and its content of a granular first class conductor costs only a fraction of the relatively expensive devices previously used. Also, there is much less maintenance and supervision where labor costs tend to be much higher in relation to the effective time of actual operation.

While the difficulties associated with prior devices for making electrical contact increase with higher wire-drawing speeds, the contacting device or method of the present invention has been proven to be relatively independent of the drawing-off speeds, thereby permitting higher transporting or drawing speeds for the wires without causing substantially greater damage or more frequent breakdowns.

The electrically conducting material employed in the roller, drum or wire contacting elements of previous devices must have a high mechanical strength as well as excellent resistance to corrosive chemicals. Because of this double requirement, the available choices of a suitable contact are narrowly limited. By comparison, the granular conducting materials of the first class employed for purposes of the present invention

do not require such a high mechanical strength and are preferably chosen primarily for their resistance to chemical attack, e.g., by the electrolyte, so that a series of previously nonuseful materials can be selected as the granular contacting means for supplying current to the transported wires.

Although the granular conductor of the invention is preferably arranged in a nonconducting container with vertical sidewalls which are slotted to receive the transported wires running horizontally therethrough, it will be recognized that this preferred construction and arrangement can be modified in various ways without departing from the more essential features of the invention. For example, the nonconducting material can be formed as a liner on a more rigid exterior shell or the side and/or end walls can be positioned at an angle to the vertical, e.g., to funnel or channel the granules downwardly while providing any suitable discharge opening at the bottom of the container. Also, the planar group of wires can be guided in somewhat different paths by means of suitable guide pins or combs, and braking or tension regulating means can be applied to the wires as well as to the feed rolls or drums from which the wires are supplied. In all cases, it is advantageous to maintain a uniform tension on the wires, substantially below their braking limit and preferably below their elastic limit so that the wires are not broken or even distorted while being transported through the contacting devices or layered zones or in the electrolytic baths. At the same time, the tension should preferably be sufficiently great to maintain a reasonably linear path of travel for each wire against the pressure exerted by the granular contact material. In many

cases, the braking tension exerted solely by the granular contact material is sufficient to yield highly satisfactory results at normal operating speeds, thereby permitting a very simple and inexpensive construction of the electrical contacting means in combination with each electrolytic treatment of the wires.

The invention is hereby claimed as follows:

1. In a process for the electrolytic treatment of a plurality of wires being transported through an electrolytic bath, the improvement for supplying electric current to said wires which comprises guiding said wires in running contact with a granular conductor of the first class arranged in at least one layered zone externally of said bath.

2. A process as claimed in claim 1 wherein the wires are passed through a layered zone of said granular conductor at each end of the electrolytic bath.

3. A process as claimed in claim 1 wherein said plurality of wires are transported at substantially parallel spaced intervals in a planar group through said bath and said at least one layered zone of the granular conductor.

4. A process as claimed in claim 3 wherein the granular conductor consists essentially of particles having a size larger than the diameter of the individual wires but smaller than the interval between adjacent parallel wires.

5. A process as claimed in claim 1 wherein said wires are transported horizontally through said granular conductor at a substantial distance below the upper surface of the layered zone.

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