

July 26, 1966

G. E. HARLAN

3,262,870

PROCESS FOR THE EXTRACTION OF COPPER

Filed Aug. 31, 1961

5 Sheets-Sheet 1

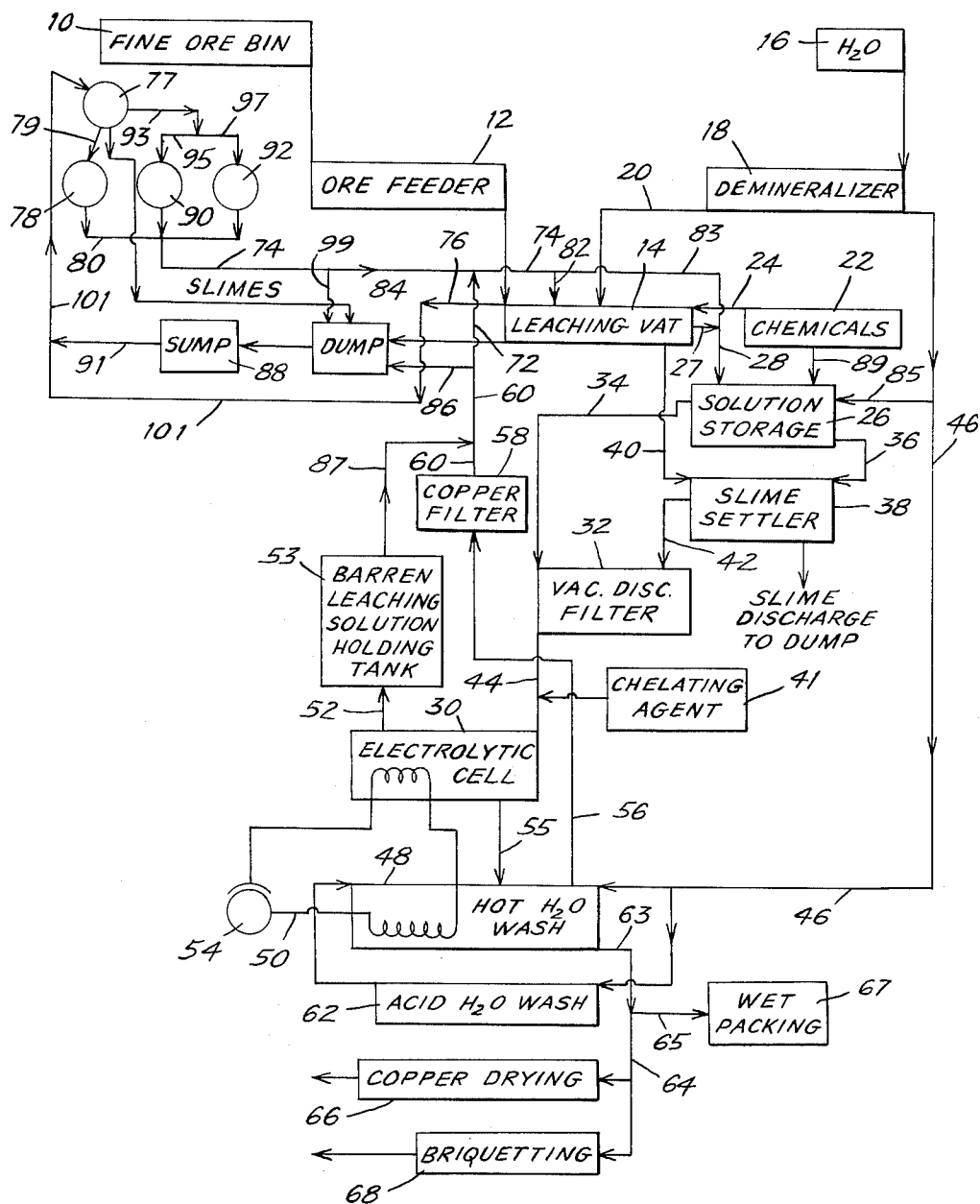


Fig. 1

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5 Sheets-Sheet 2

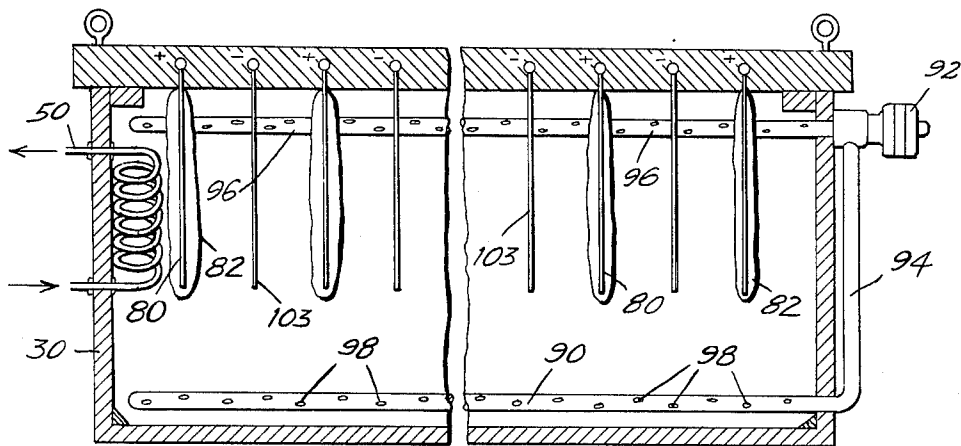


Fig. 2

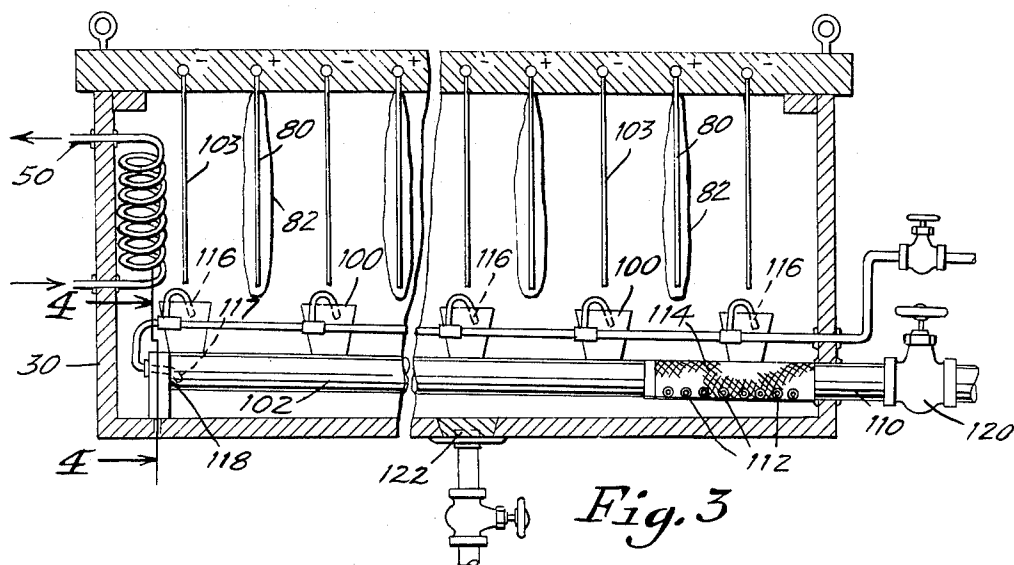


Fig. 3

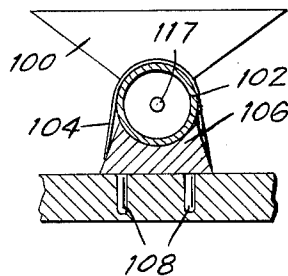


Fig. 4

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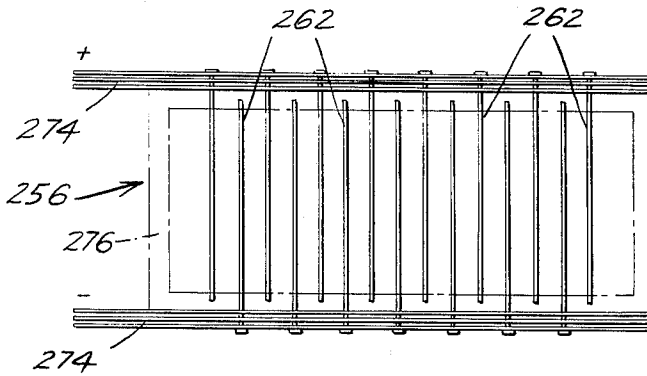
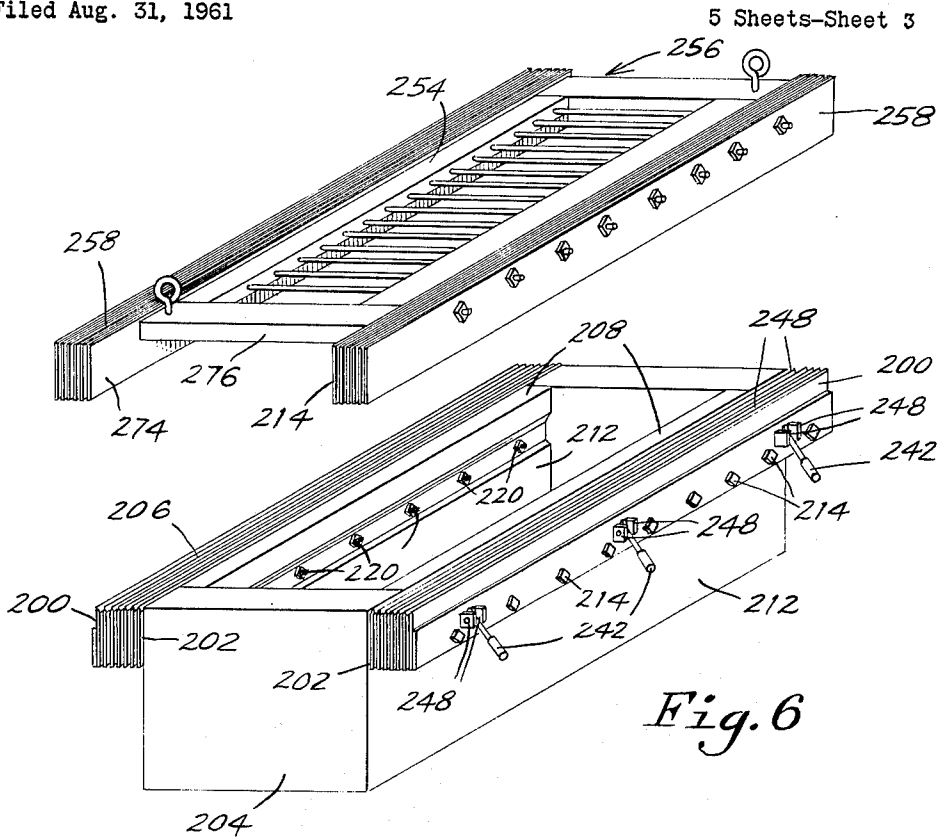
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5 Sheets-Sheet 4

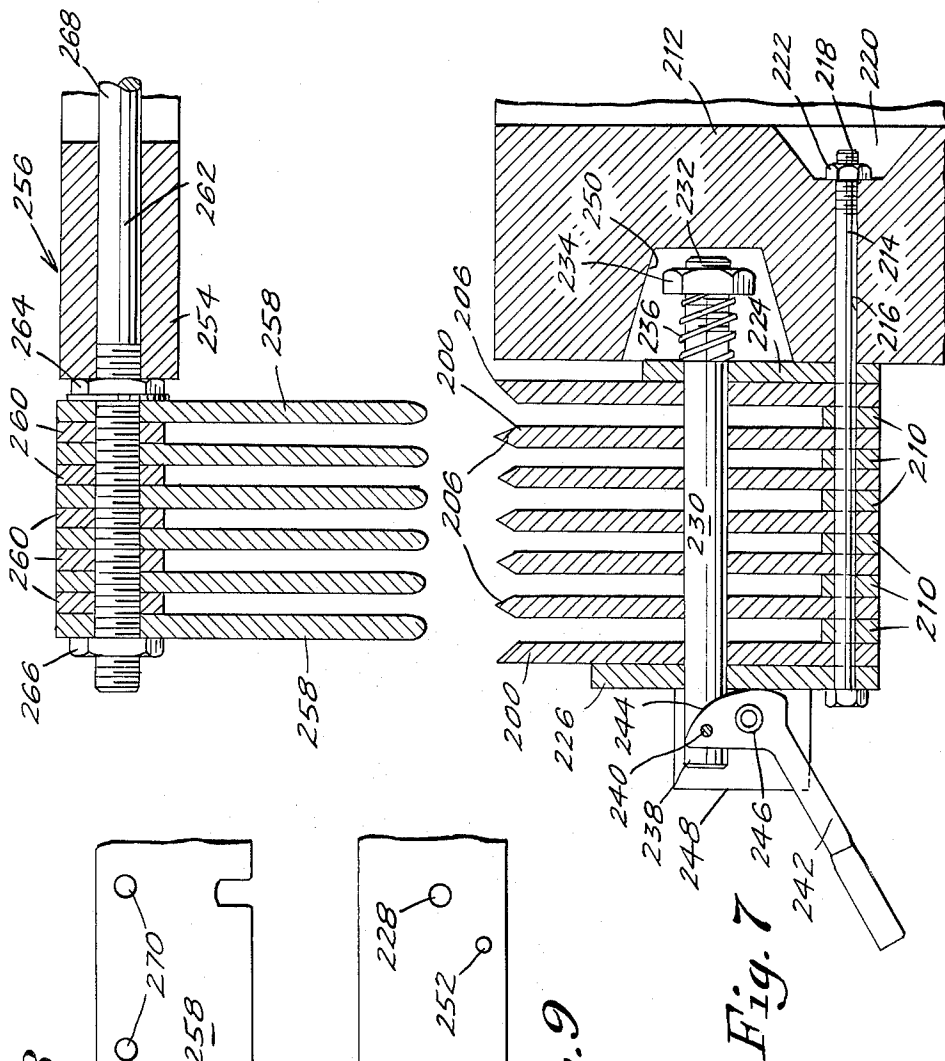


Fig. 7

Fig. 8

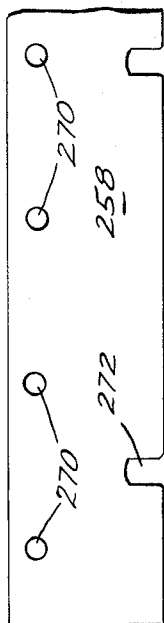
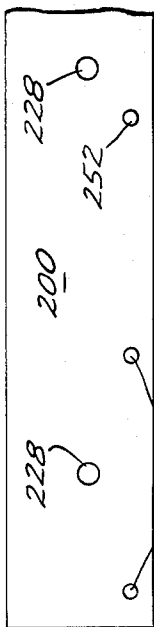


Fig. 9



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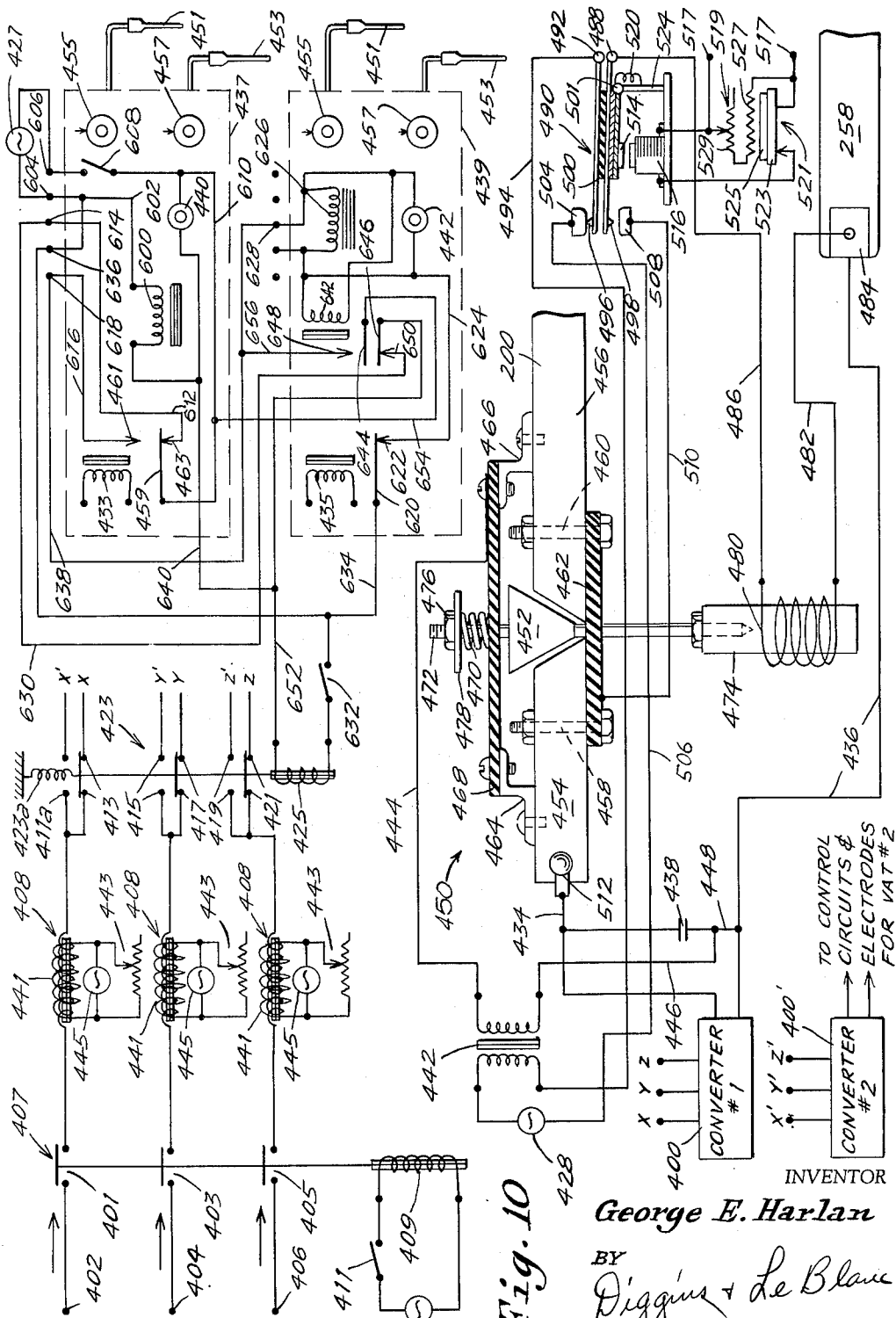
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PROCESS FOR THE EXTRACTION OF COPPER

Filed Aug. 31, 1961

5 Sheets-Sheet 5



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3,262,870

PROCESS FOR THE EXTRACTION OF COPPER
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Filed Aug. 31, 1961, Ser. No. 135,280
30 Claims. (Cl. 204-108)

This application relates to copper extraction and, more particularly, to a method of producing a high quality copper product directly from copper ore.

Notwithstanding the enormous world-wide demand for copper and the relatively extensive copper production facilities currently in operation, the present status of copper refining and extracting techniques is far from satisfactory. Currently used methods are either expensive, time consuming, incapable of producing a high quality copper product or any combination of these.

For example, one process in use today, the cementation process, involves the leaching of copper ore and the use of an iron replacement technique (utilizing sponge iron or shredded and detinned cans) to obtain an impure copper sludge which is smelted and further refined to obtain a desired copper product. In the course of this process, the leaching solution becomes contaminated with iron and must be discarded. The cost of the iron or detinned cans and of the smelting and the high cost of replacement of leaching solutions makes this process somewhat expensive considering the nature of the product which is obtained, which is far from the high purity copper which is in great demand today.

Currently known electrolytic methods of copper production, which are responsible for more than 90% of the copper produced today due to the great current demand for a higher purity copper than can be obtained by other processes, also leave much to be desired. For example, most of the known electrowinning systems, in which the pregnant liquor from the leaching vat is used as the electrolyte in the electrolytic cell, involve inordinately long leaching and copper deposition times and often result in an inferior product. In addition, they usually are extremely expensive, not only as a result of the cost of the time involved in the leaching and copper deposition cycles, which in some cases amounts to eight to thirteen days for a complete recovery cycle, but due to the high cost of reconditioning extraction materials and through wastage of large amounts of such materials. Electro-refining techniques, in which an impure copper anode, usually cast directly from a refining furnace, is utilized, are obviously inefficient due to the requirement for the preliminary refining step.

In short, there is presently a great and crying need for new and improved copper refining processes. It is the prime purpose of the present invention to produce such an improved copper refining process.

It is another objective of the present invention to provide a novel copper refining process capable of producing a high purity copper powder product directly from crude copper ore.

It is still another purpose of the present invention to provide a novel copper refining process capable of producing a copper powder product having a purity upwards of 99.5% and, if carefully controlled, as high as 99.9%, at low cost and in greatly reduced time.

It is still a further object of the present invention to provide a novel electrowinning process in which improved leaching and electrolytic extraction processes are combined into a continuous system to produce a high quality copper powder product in less time and at a significantly lower cost than is possible with currently known electrowinning systems.

It is a further object of the present invention to provide an improved leaching process with greatly increased cop-

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per extraction efficiency, both time-wise and quantity-wise, at a cost far below that of currently known leaching processes.

It is still another object of the present invention to provide an improved electrolytic extraction technique and structure for its implementation, effective to produce a high quality copper powder at significantly faster rates than currently known techniques, and in which power costs are greatly reduced.

It is still another object of the present invention to provide an electrolytic cell provided with novel electrodes capable of aiding in the production of a high purity copper powder.

It is an additional object of the present invention to provide a novel alloy useable in forming anodes capable of aiding in the production of a high purity copper powder.

It is a further object of the present invention to provide a novel electrowinning process in which electrolytic current density, voltage and electrolyte and leaching solution temperature are so correlated as to provide maximum efficiency and a high quality product.

A further object of the present invention is to provide novel means for reducing polarization in the electrolytic cell of the novel electrowinning system of the present invention.

Another object of the present invention is to provide novel structure for the efficient removal of copper powder from the cathode area in an electrolytic cell.

Still another object of the present invention is to provide a novel bus-bar assembly for use in conjunction with the electrolytic cell used in the practice of the present invention.

These and other objects and advantages of the present invention will become more apparent upon reference to the following description and appended claims and drawings wherein:

FIGURE 1 is a flow diagram illustrating the various stages of production of the novel copper extraction process of the present invention;

FIGURE 2 is a schematic diagram illustrating the electrode connections of an electrolytic cell employed in connection with the present invention;

FIGURE 3 is a transverse vertical section through an electrolytic cell illustrating a novel collecting device for removing copper powder from the area of the cathodes;

FIGURE 4 is a partial transverse sectional view showing details of the structure of the collecting device of FIGURE 3, taken along line 4-4 of FIGURE 3, but omitting piping for clarity of illustration;

FIGURE 5 is a top plan view in schematic of a hanger frame used in connection with the electrolytic cell of the present invention, illustrating the mounting of the electrodes and female bus-bars and showing the hanger frame in phantom;

FIGURE 6 is a perspective view of an electrolytic cell illustrating the positioning of the male and female bus-bar assemblies;

FIGURE 7 is an end elevation of the male and female bus-bar assemblies of the present invention;

FIGURE 8 is a front elevation of a male bus-bar in reduced scale for purposes of illustration;

FIGURE 9 is a front elevation of a female bus-bar in reduced scale for purposes of illustration; and

FIGURE 10 illustrates a novel depolarizer system utilized in connection with the present invention, in partial section.

A general understanding of the overall nature of the novel electrowinning process of the present invention may best be obtained by reference to the flow diagram illustrated in FIGURE 1. Details of the individual process steps will be provided at a later point in this specification.

Ore of the desired particle size (which has been dressed by conventional methods) passes from bin 10 into ore feeder 12 from which it is fed into leaching vat 14. Water from 16 is demineralized at 18 and is fed into leaching vat 14 through line 20. Chemicals are then fed into leaching vat 14 from storage 22 through line 24.

After the ore in leaching vat 14 has been leached sufficiently, the ore is drained of pregnant leaching solution which passes into solution storage tank 26 through lines 27 and 28. As shown, line 28 permits drainage of pregnant leaching solution slightly above the ore level to achieve maximum clarity of solution. After solution storage tank 26 has been filled to capacity and as needed for the operation of electrolytic cell 30, the cleanest portion of the pregnant solution is decanted from the upper level of solution storage tank 26 (slightly above its midpoint) and is fed into a vacuum disc filter 32 through line 34 to produce a sparkling liquor. The portion of the pregnant solution in the lower level of solution storage tank 26, which contains considerable slimes, is then permitted to flow through line 36 into slime settling tank 38. Additional slime is fed into slime settling tank 38 through a drain-off line 40 connected to a false bottom (not shown) in ore leaching vat 14, though slime from the leaching vat preferably is not drained at the same time that pregnant solution is flowing in any of lines 28, 34 or 36.

When the slimes have settled to the bottom of settling tank 38, the slime-free solution from the tank may be fed into vacuum disc filter 32 through line 42 (located above the settled slimes) to supplement the upper level solution fed to said filter through line 34. This filtering step is important to avoid contamination of the electro-deposited copper powder by undissolved particles (i.e., magnetite and gangue material) which may be entrained in the solution. Slimes discharged from settling tank 38 are sent to the dump, but are not mixed with the tailings from leaching vat 14, which have been sent to the dump (see below) for further copper extraction, so as to avoid cementing the tailings.

Filtered pregnant solution, which may have a chelating agent added to it as at 41, is then fed into the electrolytic cell 30 through line 44 for the electrolytic extraction of the copper in the charged solution. At this point, and before the start of the electrolytic extraction process, demineralized water is fed from tank 18 through line 46 into hot water wash tank 48 so as to take advantage of Joule effect heating in electrolytic cell 30 through heat exchanger 50.

After the desired quantity of copper deposition has taken place in electrolytic cell 30, spent (barren) solution from cell 30 is passed through line 52 to holding tank 53 for reuse in leaching the next charge of copper-rich ore in leaching vat 14 (see below).

After the spent solution has been drained from electrolytic cell 30, the copper pulp (which, as near as can be detected, may be as fine as 1-25 microns in size) in the bottom of the cell is discharged through a novel discharge system to be described hereinafter through line 55 into hot water wash tank 48, where it receives its first wash in deaerated, hot, pure water. As indicated above, this water is heated by means of heat exchanger 50 (to at least about 200° F.) which has heat exchange coils in hot water wash tank 48 and electrolytic cell 30. Heat exchange fluid is circulated in heat exchanger 50 by means of a small pump 54. Care must be taken to control the quantity of wash water added so that the copper pulp-wash water mixture does not reach a pH greater than about 6.0 at the termination of the washing step; otherwise oxidation would take place.

This first, hot water wash is extremely important inasmuch as it has a marked effect in the stabilization of the copper, effects the removal of oxidized particles and of gas, considerably lessens the copper powder settling time, and reduces to a minimum the loss of chemicals and cop-

per. If this procedure is not followed, gases (i.e., SO₂) may eventually destroy the furnaces in which the copper is dried.

After the copper pulp in wash tank 48 has been thoroughly agitated and washed in this first hot wash water for approximately one-half hour, this water, which has accumulated trace copper and trace chemicals which have been washed from the copper pulp, is removed from the copper pulp through line 56 and passed through a fine copper filter unit 58 to remove entrained solids. The filtered first wash water is then fed into line 60 for a purpose to be described below.

If the copper is to be packed or shipped as wet pulp, the copper pulp is then washed for a second time in wash tank 48 by means of an aqueous acid wash (i.e., aqueous sulfuric acid of pH 4.0-5.5) fed into tank 48 from acid wash tank 62. The purpose of this acid wash is to stabilize the copper pulp to prevent it from oxidizing. Only enough acid wash is used to completely cover the pulp. After the copper pulp in tank 48 has been agitated and washed in the second wash water, the acid wash-covered copper pulp is removed through lines 63 and 65 and wet-packed at 67.

In the event the copper is not to be packed or shipped as wet pulp, the second wash in acidified water is omitted. In lieu thereof, the copper pulp is given a hot water wash (with demineralized water) in tank 48 similar to the first wash, the contents of the tank being thoroughly agitated during this washing step. Following this washing, the wash water is removed from tank 48 through line 56, passed through filter unit 58 to remove entrained solids, and fed into line 60 for a purpose to be described below.

The wet copper pulp is then removed from tank 48 through lines 63 and 64 and dried at 66. The drying may best be accomplished by charging the wet powder into a suitable furnace and, using a hydrogen atmosphere, drying the powder and continuing to increase the temperature up to the desired presintering temperature, which is approximately 495° C. In this way, drying and presintering may be accomplished in the same operation, and excellent results are obtained.

In lieu of the treatment in furnace 66, the wet powder may be briquetted in a conventional manner as at 68.

As stated above, after the first hot wash, water is passed through filter unit 58 to remove entrained solids, the water is fed into line 60. From line 60, this water is passed through lines 72 and 74 and into leaching vat 14 which, as above described, has previously been drained of pregnant leaching solution. This wash water is then passed upwardly through the ore tailings in the leaching vat (in the same manner in which the original leaching solution is passed through the unleached ore, as set forth below) to further remove soluble copper from the tailings, which, in many cases, may still contain as much as 30% of the original soluble copper content of the ore. In the average case, this wash will remove about 20% of the soluble copper remaining in the tailings. When this wash has been completed, the slightly copper-enriched wash water is removed from the leaching vat through lines 76 and 101 and passed into slime settling tank 77, from which clear solution is removed through line 79 and directed into storage tank 78.

Since a given commercial batch of pregnant leaching solution (viz., that obtained from the leaching of a single batch of ore) will undoubtedly be subjected to electrolysis in a plurality of electrolytic cells, there will be a plurality of first wash waters available for the washing of the ore tailings. Each of these first wash waters is passed upwardly through the tailings in the manner described above and eventually passed into storage tank 78 in which it is mixed with previously stored first wash waters.

The stored first wash waters in tank 78 may subsequently be utilized to further wash the tailings in leaching vat 14 (in the manner described above) to further remove soluble copper from the tailings. For this purpose, the

stored first wash waters are removed from tank 78 and passed into vat 14 through lines 80, 74 and 82. Such further treatment utilizing the stored first wash waters will eventually build up the copper content of these wash waters to a point at which they may be used as the pregnant solution for the electrodeposition of copper powder. For such purpose, the pregnant first wash waters would be withdrawn from tank 78 through lines 80, 74, 83 and 28 and passed into solution storage tank 26, in which tank the charged solution is treated as was the original charged solution (see above). As indicated in FIGURE 1, demineralized water and/or chemicals may be added through lines 85 and 89, respectively, if needed to bring the constituency of this pregnant solution within the limits set forth for the barren solution make-up described below.

In general, it will not be commercially practicable to subject the pregnant first wash water accumulation to electrolysis until its copper content has increased at least to 25 grams per liter of solution. The highest practicable copper content for use in the electrolytic cell is 45 grams of copper per liter of solution.

Following the washing of the tailings with the first wash waters, the washed tailings, still containing soluble or entrained copper, are removed from the leaching vat and deposited in dump 84.

The wash water described above as being used in lieu of the acid water wash (the former will hereinafter be referred to as the second water wash), after being passed through filter 58 to remove entrained solid particles, is passed through lines 60 and 86 and poured over the tailings (or slimes) in dump 84. The tailings (or slimes) will then be allowed to soak in this second water wash for the removal of further amounts of soluble copper still retained by the tailings (or slimes). The enriched second wash water will slowly drain from the tailings (or slimes) into a drainage ditch (not shown) and into sump 88, from which it will be conveyed through lines 91 and 101 to slime settling tank 77 for removal of slimes and through lines 93 and 95 or 97 to storage tanks 90 or 92. Since, as was stated above in connection with the first wash waters, a plurality of electrolytic cells will probably be utilized in the commercial treatment of a given batch of pregnant leaching solution, a plurality of second wash waters will be available for soaking the tailings (or slimes) in dump 84, all of which will eventually drain off and be transported to storage tanks 90 and 92.

The second wash waters in tanks 90 and 92 may then be utilized, as necessary, to aid in the washing of the tailings in vat 14 (as was the case with the first wash waters), after which these wash waters will be returned through lines 76 and 101, slime settling tank 77, line 93, and lines 95 and/or 97, to tank 90 and/or 92. Alternatively, the second wash waters in tanks 90 and 92 may be used to further wash the tailings (or slimes) in dump 84, in which case the wash waters will be removed (by gravity feed) through line 99, directed into dump 84, drained off into sump 88, and returned to tanks 90 and 92 through lines 91 and 101, slime settling tank 77, line 93 and lines 95 or 97. When the copper content of the second wash waters is within the ranges set forth above in connection with the first wash waters, it may then be utilized as a new charge for the electrolytic cell in a manner similar to that in which the charged first wash waters were so used.

If desired, the copper pulp in tank 48 may be given additional hot, deaerated, demineralized water washes to remove gases, chemicals, impurities, etc., if this is deemed necessary. These wash waters, following the washing step, may be utilized as were the first and second wash waters, and additional storage tanks may be provided for them, if desired.

As stated above, after the spent, barren solution is removed from the electrolytic cell 30, it is stored in holding tank 53 for reuse in leaching the next charge of copper-rich ore in leaching vat 14. For this purpose, it is passed

through lines 87, 60, 72, 74, and 82 into the vat 14. Since about 3-5% of the original make-up will be lost in the conduct of a complete cycle, additional demineralized water and chemicals must be added to bring the new make-up constituency within the limits set forth below for the barren solution make-up.

In the description set forth above, a general outline of the process of the present invention was set forth. For fuller understanding of the present invention, however, details of the various aspects of this process and of apparatus for its use are set forth below.

The leaching method which is employed in carrying out the process of the instant invention utilizes a forced upward circulation technique, the continued upward circulation of the leaching solution affording upward percolation for fast leaching of the ore. Unless upward circulation (viz., passage of the leaching solution up through the ore) is employed, many problems will arise, since downward circulation will cause cementation of the false bottom in the leaching vat and prevent the ore from serving as a filter. Upward circulation causes slimes and fines to move upwardly, leaving coarser material at the bottom of the vat to serve as a filter bed. Good circulation is obtained by recycling about 5% of the total volume of the leaching solution per minute.

Unlike most agitation system requirements, the leaching system of the present invention does not require crushing and grinding of the raw ore to the usual extent. Indeed, one of the great economies afforded by the present invention is effected through elimination of the necessity for high cost grinding equipment and operations. Preferably, ore particle size should be as follows: not more than 5% by weight of the ore should be coarser than $\frac{1}{4}$ " mesh; not more than 50% of the total ore content should be coarser than 20 mesh (U.S. Standard Sieve). The ore may be ground to size by conventional methods.

The nature of the leaching solution is determined not only by the particular ore which is to be leached but by the requirements of the electrolytic cell. For example, the leaching solution must be so formulated as to extract at least a certain minimum quantity of copper from the ore, so that a minimum quantity of anions will be present to keep the copper ions in suspension in the electrolytic cell, so as to eliminate or render impotent impurities which would otherwise cause undesirable cell reactions, etc.

The basic ingredients of the leaching solution are sulfuric acid and water. For each approximately 1815 parts by weight of water, the leaching solution should contain approximately 175-190 parts by weight of concentrated sulfuric acid (approximately 93-95%, 1.84 specific gravity, 66° Baumé). In other words, the sulfuric acid content of the leaching solution should be approximately 8-9% by weight of the solution. If the acid content is much more than 190 parts by weight, it will interfere with the operation of the electrolytic process; if it is much below 175 parts by weight, the characteristics of the copper product may be altered and the electrodeposition time may be increased. Highly superior results are obtained with a mixture of approximately 1815 parts by weight of the water and approximately 180 parts by weight of the acid.

The demineralized water for the leaching solution may be mildly alkaline, but the alkalinity should be kept to the lowest possible minimum since alkali dilutes or bases the action of other ingredients in the leaching solution. In addition, the water should be tested before use in the leaching process with a silver nitrate solution to ascertain the presence of sodium chloride or any other chlorides, which may be detrimental to the successful carrying out of the electrowinning process and should be removed by conventional techniques. The water should also preferably be free of calcium, magnesium and iron.

In addition to the foregoing, various additives should

be included in the leaching solution before the leaching step takes place. For example, it is extremely desirable to have alumina in the solution not only to serve as a catalyst for accelerating the deposition of copper in the electrolytic cell but also to serve as an electron promoter under certain conditions. It is desirable to have approximately 1 part by weight of alumina in the sulfuric acid solution described above. When average copper ores are used, this amount of alumina can, in most cases, be leached into the solution without the necessity for a separate alumina addition. Accordingly, the ore should be tested prior to the leaching step to determine the quantity of alumina which can be expected to be extracted by the leaching solution. If sufficient alumina to provide the desired quantity is not present, the difference should be added to the leaching solution prior to the leaching step.

If much calcite (CaCO_3) is present in the copper ore to be leached, it may be beneficial to add sodium sulfate to the charged, filtered solution to compensate for the SO_4^{--} ions taken out of solution through the formation of insoluble CaSO_4 . If the calcite is present only in a trace amount, of course, this additive may not be necessary. Whether or not the sodium sulfate should be added can be determined by conventional pilot plant tests. Usually, calcite does not build up to troublesome proportions until the leaching solution has been recycled five or six times. The addition of sodium sulfate can be extremely important in maintaining a balanced equilibrium between the anions and cations in the electrolyzed solution in supplying the necessary SO_4^{--} ions.

In the leaching of copper from copper ore by means of the above-described leaching solution, significant quantities of iron may often be leached into the solution along with the copper, though it should be noted that the dilute leaching solution used in the present invention has a much greater tendency to dissolve copper than it does the complex iron compounds in the ore, resulting in an efficient yet short leaching cycle without undue build-up of iron. Small, controlled amounts of ferrous iron which converts to ferric iron in the electrolyte solution may be extremely beneficial not only in complexing calcium and magnesium salts (to salt them out of solution) but in maintaining the peroxide coating on the anode (see below) and in preventing and controlling excessive polarization of the cell electrodes. As is well known, if polarization is permitted to build up in an uncontrolled manner, cell deposition efficiency may be significantly decreased. Despite this advantage, free ferric iron in the electrolyte solution may be extremely harmful if present in excessive quantities, inasmuch as the excess may react with the copper in solution to render it impure with iron. Insofar as copper purity is concerned, no more than about 5 grams of ferric iron per gallon of electrolyte should be present to obtain 99+ % pure copper; to obtain the highest purity copper (99.9 %), no more than 2 grams of ferric iron per gallon should be present.

To eliminate the potentially harmful effects of ferric iron in the electrolyte solution while retaining some of the benefits of the iron, the present invention contemplates the addition of chelating and complexing chemical agents to the pregnant electrolyte solutions. The first of these is the chelating agent known in the trade as Versene Fe-3 Specific, 34% Liquid, which is a tetrasodium salt of ethylenediamine tetraacetic acid. When preacidified to a pH of between approximately 4 and 5 (i.e., by a 5% solution of sulfuric acid), 7.08 gms. of the Versene Fe-3 Specific will chelate approximately 2.055 gms. of ferric iron.

In general not more than approximately 1.85 gms. of Versene Fe-3 Specific should be used per liter of pregnant solution. If more than this amount is used, the peroxide coating on the anodes (see below) may be destroyed and an undesirable substitute formed. More specifically, an undesirable excess of the Versene Fe-3 Specific may cause the lead of the anode to form lead sulfate (which is, at

best, only a semi-conductor) in the presence of the sulfuric acid of the electrolyte, resulting in diminished anode conductivity, increasing the electrodeposition time and resulting in the contamination of the copper pulp product. Excess Versene Fe-3 Specific may also cause lead sulfate to cement up the anode bag (see below) to decrease its porosity, resulting in increased deposition time and possible contamination of the copper pulp product.

In the event that approximately 1.85 gms. of Versene Fe-3 Specific per liter of pregnant solution is insufficient to chelate the total iron content of the solution (except, of course, for the trace of iron which, as pointed out above, is desirable), phosphoric acid may be added as a second chelating agent. The phosphoric acid will serve to complex the ferric iron in the electrolyte solution without causing any undesirable reactions at the time of its addition or during the electrolytic stage of the process. In general, approximately 0.75 cc. of 85% orthophosphoric acid will be sufficient to complex 0.62 gram of ferric iron per gallon of solution.

As stated above, a slight amount of ferrous iron in the electrolyte solution is beneficial, about 100-500 mg. of ferrous iron per liter of electrolyte solution preferably being present for most desirable results. To assure the presence of this minimum quantity of ferrous iron, an iron analysis should be made on the pregnant leaching solution (viz., after the copper has been leached from the ore) to determine the quantity of soluble iron which has been leached into solution. If the quantity of ferrous and ferric iron present is greater than approximately 100-500 mg. per liter of solution, sufficient Versene Fe-3 Specific should be added to complex the excess ferric iron. If the amount of excess ferric iron is sufficiently great so that 1.85 gms. of Versene Fe-3 Specific per liter of solution will not completely complex the excess, the remaining portion of the excess should be complexed by means of the phosphoric acid additive, as described above. Preferably, the Versene Fe-3 Specific and phosphoric acid (if used) should be added directly to the pregnant leaching solution after the solution has been filtered in vacuum disc filter 32 (see FIGURE 1).

One of the primary advantages of the present invention is that it makes possible the use of dressed oxidized copper ore without the necessity for preleaching treatment, which is usually required in conventional, current-day extraction processes. Where oxidized copper ore is not utilized, however (i.e., where sulfide ores are used), it may be necessary to roast or sulfatize the ore before the leaching step.

The present process is capable of treating all oxidized copper ores, including but not limited to cuprite, malachite, chrysocolla, azurite, tenorite, brochantite (contains some oxide with sulfates), and calcanthite (copper sulfate ore). For commercially effective results, the ore should have at least about 2% by weight of copper and no more than the listed maximum percent by weight of the following ingredients:

Soluble iron	5.0
Lime (as active CaO)	5.0
Alumina	20
Silica	80
Chlorides	* 1.0
Zinc	* 1.0
Antimony	* 1.0
Lead (red lead oxide)	0.1
Molybdenum	0.1
Fluorides	0.02

* And preferably less.

For copper ores containing leachable copper of less than approximately 4.75 weight percent by assay, about one ton of leaching solution per ton of ore should be used. If the leachable copper in the copper ore ranges from approximately 4.75 to 7.50% by weight, approximately 1½ tons of leaching solution should be used per

ton of ore. For copper ore containing leachable copper in a quantity of approximately 7.50% to 10% by weight, approximately 2 tons of leaching solution per ton of ore should be employed. If the ore contains leachable copper in excess of 10%, it may be desirable to run the leached ore through another charge of fresh barren solution. The quantity of copper in the ore may be determined, of course, by conventional techniques.

The temperature of the leaching solution should be approximately 110–130° F. and best results are obtained when the temperature of the leaching solution is 130° F. As will become apparent hereinafter, the heat to raise the leaching solution to this temperature is supplied through Joule effect heating in the electrolytic cell.

The leaching time will vary depending upon the nature and particle size of the ore used. In general, leaching with a given batch of leaching solution should continue until about 25–45 grams of copper per liter of solution have been extracted from the ore. Tests have indicated that, for an average batch of ore, the leaching time will vary from 40 minutes to 1½ hours. Care must be taken not to extend the leaching step over too long a period of time since excessive leaching will extract excessive amounts of various impurities (i.e., iron, calcium) which may preclude the obtention of high purity (viz., 99.9%) copper. (This is the primary reason for setting an upper limit of approximately 45 gms./liter as the amount of copper to be extracted from the ore for the initial leaching step.) The preferred leaching time is 40 minutes to one hour in most cases.

The electrolytic cell used in conjunction with the leaching process described above has many novel and important features. As shown in FIGURE 2, a parallel electrode arrangement is employed, all of the cathodes in a given cell being connected in parallel with one another and all of the anodes in one cell being similarly connected in parallel with one another.

Of critical importance are the particular electrode compositions. The anodes (designated by the numeral 80 in FIGURES 2 and 3) are fabricated of pure soft lead alloyed with extremely pure antimony, the lead being present in a range of approximately 88 to 91% by weight with the antimony being present in a range of approximately 12–9% by weight. Impurities such as silver, copper, zinc, arsenic, iron and bismuth should be present in no greater than trace quantities. Preferable maximum impurity limits in the anode alloy are approximately as follows: silver—.0004%; copper—.0009%; zinc—.0005%; arsenic—.0003%; iron—.0002%; bismuth—.0014%.

The lead-antimony composition limits set forth above are absolutely necessary to the successful operation of the process of the present invention. For example, a lead-antimony alloy richer in antimony (i.e. 87 Pb–13 Sb) will dissolve at an excessive rate, contaminating the copper pulp product with lead and necessitating more frequent anode replacement. Lead-antimony alloys lower in antimony (i.e., 92 Pb–8 Sb) are also unsuitable for the carrying out of the process of the present invention under optimum conditions. Such a low antimony content electrode is incompatible with the various conditions which must be maintained in the electrowinning system such as the required electrolyte solution temperature affording maximum efficiency for a short-time leaching cycle, permitting the diminution of cell resistance and affording more rapid deposition of a bright, low oxygen-content copper powder.

In addition, such a low antimony content would pose extreme difficulties in the light of the high current density required for the best and most efficient copper powder deposition and the reaction effect of the chelating agent which is used to complex excessive iron extracted from the copper ore. With respect to the latter effect, the use of a low antimony content alloy may result in the formation of lead salts on the anode which, in turn, may

result in copper powder contamination. In addition, a low antimony content anode may react with the tetraacetic acid constituent of the Versenate. A too low antimony content and/or impure lead may also cause an undue temperature rise, which would cause the electrolyte in the vicinity of the anode to boil at the current densities used in the present invention.

A particularly desirable anode is a 90 Pb–10 Sb alloy having no more impurities than the maximum limits set forth above.

Most effective results have been obtained in the copper deposition process of the present invention through utilization of cathodes (designated by the numeral 103 in FIGURES 2 and 3) fabricated of 99% pure rolled nickel sheet. Such a cathode has a high affinity per a given surface area for hydrogen gas (the more gaseous the cathode is, the more efficient it is in producing fine copper powder). In addition, the nickel is substantially non-corrodible, both with respect to the electrolyte and the fumes which are invariably produced in the cell space above the electrolyte, and is substantially self-cleaning on the deposition surface area.

The portion of the surface area of each anode which is immersed in the electrolyte should preferably be smaller than the corresponding immersed surface area of each of the cathodes. If the immersed surface areas are the same, large trees of copper will tend to form around the immersed edges of the cathodes. Preferably, the anodes should be approximately one inch shorter on each of their immersed edges than the cathodes. Tree formation can also be minimized by rounding the edges of the cathodes.

For a practical commercial structure, the cathodes should preferably be approximately 32" wide, 40" long and ¼" thick; the anodes should be approximately 30" wide, 39" long and ½" thick. Approximately 4" of the length of each of the anodes and cathodes will not be immersed in the electrolyte to permit them to be hung from a hanger structure above the electrolyte.

A practicable commercial cell may utilize 9 anodes and 8 cathodes, though the number of electrodes may be varied if desired. Preferably, the electrodes at the ends of the cell should be anodes. It should be noted, however, that cathodes have been shown at the ends of the cell illustrated in FIGURE 3 solely for clarity of illustration. Electrode spacing should be approximately 2¾" to 3¼". Electrode spacing near the lower limit will tend to produce more finely divided copper powder; that nearer the upper limit will tend to produce a more granular product. In a cell of the type described, approximately 1140 to 1175 gallons of electrolyte should be present.

As shown in FIGURES 2 and 3, each anode is encased within an anode bag 82. These anode bags act as diaphragms which permit electrolyte to diffuse through them fairly slowly, resulting in the limiting of the free flow of the acidic electrolyte towards the anodes. The oxidizing action of the anodes is sufficiently strong as to have a tendency to base the electrolyte immediately adjacent it, thus assisting in the liberation as a gas of any chlorine, fluorine or other harmful materials from the electrolyte, should they be present. If chlorine, fluorine, etc., are present in the electrolyte and not removed, the copper powder which is electrodeposited may be contaminated. In addition, the anode bags also serve to filter or trap particles or substances (such as salts) formed at the anode which would otherwise contaminate the electrolyte solution and the copper powder dropping to the bottom of the electrolytic cell. Still further, the anode bags limit or prevent the ferrous iron in the solution from being oxidized too rapidly to the ferric iron formed by means of the diffusion action of the bags, which suppress the free flow of solution to the anode compartment to a great degree.

The anode bag must be made of a material which is

non-shrinking. If shrinkable material were used under the high current conditions employed in the use of the process of the present invention, excess heat would be produced and excess oxidation would take place at the anode.

An extremely satisfactory anode bag may be fabricated of a material made from Dynel-Vinyon, VN-753, which material is made from a copolymer of vinyl acetate and vinyl chloride.

For optimum cell operation, the anode bags should occasionally be removed from the anodes and washed in pure water.

For best results, the anode should bear a coating of lead peroxide; otherwise, lead sulfate will accumulate and contaminate the copper powder under certain electrochemical conditions which may exist during the conduct of the process. This peroxide is best formed on the face of the anodes by their pretreatment in an electrolytic cell containing an electrolyte having a small amount of aqueous ferrous sulfate.

The cathode current densities employed in connection with the present invention are important for a number of reasons. Not only does the high cathode current density employed ensure the deposition of a copper powder of highly satisfactory constituency but, in addition, such current density coordinates the copper powder deposition cycle with a rapid ore leaching cycle, produces the proper I²R effect which will develop the required temperature rise in the spent electrolyte (which is later utilized in the leaching of the ore), which, in turn, affords increased penetration of the leaching solution into the ores. The cathode current density should be approximately 125 amps./ft.² (per cathode side) at the beginning of the electrolytic cycle, the current density gradually tapering upward to approximately 250 amps./ft.² (per cathode side) at the finish and automatic cut-off point of the cell operation.

In general, the anode current density will lag behind the cathode current density at any given time by approximately 5% over the entire electrodeposition cycle.

The starting voltage between electrode pairs should preferably be approximately 7.5 volts but should not exceed approximately 8.0 volts in any event. As the process proceeds and the current density increases as above described, the electrode voltage will gradually taper downwardly to a minimum of approximately 6.25 volts. Voltage lower than this minimum will not give satisfactory results in the process of the present invention for a number of reasons. Thus, research has demonstrated that the use of a voltage below 6.25 tends to develop an unstable condition in the copper deposition process, viz., part of the copper which is deposited will be in either solid or paste form, which may be substantially oxidized, and part will be powder, and the color and oxygen content of the powder will be affected considerably. In addition, the temperature rise required for satisfactory and fast deposition of bright copper powder will be retarded due to the reduction in the I²R effect within the electrolyte (the current will be too low).

The density of the electrolyte in the electrolytic cell must be controlled at all times so that the desired electrical conductivity limits are maintained and so that the SO₄[—] ions will keep the copper ions in suspension. The minimum copper content of the electrolyte should never fall below approximately 15 grams per liter of electrolyte for the best cell control. Failure to exercise such control will impair the particle size and shape of the deposited copper pulp as well as the efficiency of the entire process. When the copper content of the electrolyte falls below 15 grams per liter, current is wasted in liberating hydrogen from the electrolyte and in splitting and diluting the components of the electrolyte, and results in a deposit of darkened copper pulp on the cathodes. The latter results through a loss of hydrogen at the surface of the cathodes,

permitting a greater amount of oxygen to combine with the fine copper pulp. In view of the above, automatic controls should be provided to automatically terminate the electrolytic process when the copper content of the electrolyte falls below 15 grams per liter. For most efficient overall operation, the initial copper content of the electrolyte should be approximately between 25 and 45 grams per liter.

Similarly, the free acid content of the electrolyte should never fall below 45 grams per liter of electrolyte for most effective operation of the cell. The maximum free acid content of the electrolyte should not exceed 100 grams per liter and preferably not be above 90 grams per liter.

Also essential for maximum leaching cycle-electrolytic cell overall process efficiency is the operating temperature of the electrolytic solution. For optimum results, the temperature of the electrolyte should be from approximately 15 to 60° C. and the system should be set to cut off current flow to the electrolytic cell when the temperature reaches the 60° C. maximum. Preferably, the maximum temperature should not exceed 55° C. The increase in temperature in the cell not only serves to provide heat for the leaching solution to vastly decrease leaching time but serves as well to effect the deposition of a highly desirable, bright copper powder and to preheat the copper pulp wash water.

Each electrolytic cell used in connection with the system of the present invention employs agitators or pumps to circulate the electrolyte from the cell bottom upwardly and between the electrodes so as to increase the electrodeposition efficiency, decrease polarization and to assist removal of the copper from the electrodes. Upward circulation of the electrolyte also prevents stratification or splitting of the solution of the electrolyte, which splitting would impair uniform deposition of powder over the collecting surface of the cathodes and result in unbalanced current distribution over such surface area. Such agitation saves current which otherwise would be consumed in setting gas free. If the electrolyte is circulated downwardly (viz., from header 98 to header 90), the electrolyte will tend to migrate to the peripheral electrode areas without passing between electrodes and temperature and electrolyte stratification will result.

In view of the above, the specific rate and direction of circulation or agitation of the electrolyte is extremely important. If it is too low in flow of gallons per minute, excessive hydrogen will be liberated as a gas at the cathode, causing electrical current to be wasted in the liberation of gas rather than in the deposition of copper. In addition, copper deposition may be slowed and excessive polarization and electrolyte stratification may take place. If the circulation rate is too high, there will be serious danger of obtaining an inferior copper powder product, or the production of a portion of the copper as a solid on the cathode and only part as powder. Furthermore, too high circulation may decrease deposition efficiency. In general, a circulation rate (in gallons per minute) approximately 10% of the volume of the electrolyte in the electrolytic cell is adequate for efficient and rapid deposition of copper powder.

Preferably, the circulation solution intake line or tubing should be located near the top of the cell, as shown in FIGURE 2 at 96, and a small pump 92 provided outside the cell to pump the solution downwardly through tubing 94 located at the end of and running diagonally downwardly and across the cell. This tubing terminates in a solution discharge pipe or line 90 containing discharge orifices 98 which discharge the solution slowly upwardly and near the edges of the electrodes. This method provides for extremely uniform distribution of solution from the entire bottom of the cell on one side to a diagonally opposite point at the top of the cell, resulting in highly satisfactory electrolyte circulation.

Of special significance in the process of the present invention is the heat economy obtainable through the

particular heat exchange system which is employed. As previously indicated, the I²R heating effect in the electrolytic cell during its operation will serve to heat the electrolyte to a temperature of from 15 to 60° C. Since the spent electrolyte is ultimately returned to the leaching vat for a new leaching cycle following the termination of the electrolytic cycle, the heating effect of the electrolysis is fully utilized and the leaching cycle accelerated through the use of a higher temperature leaching solution. At the same time, the use of heat exchanger 50 (see FIGURES 1 and 2) connecting the electrolytic cell 30 and the wash tank 48 utilizes the heating effect in the cell to heat the first wash water in tank 48.

Of further significance is the particular copper pulp removal system utilized in connection with the above-described electrolytic cell. As clearly shown in FIGURES 3 and 4, the novel pulp removal structure comprises a plurality of rubber or plastic hoppers 100 mounted on and in communication with a powder discharge conduit 102, one such trough being situated beneath each cathode 103. Conduit 102 is mounted at its end at the base of the electrolytic cell 30 by means of an end strap 104 secured to a support 106 which is pinned into the cell bottom by means of wooden pins 108. The other end of conduit 102 is supported within an aperture 110 in one side of the cell 30.

Discharge conduit 102 is inclined as shown in FIGURE 3, the lower portion of the conduit being provided with a plurality of apertures 112 to permit entrained spent electrolyte to drain from the copper powder within the hoppers 100 and/or conduit 102. This portion of conduit 102 is covered with a chemical-proof cloth 114, such as the Dynel-Vinyon, VN-753, material used for the anode bags heretofore described, to prevent copper pulp from also discharging through apertures 112. The apparatus is also provided with a plurality of overhead pure water nozzles 116 and an end nozzle 117 directed respectively into hoppers 100 and into the end 118 of conduit 102 for flushing the powder out of the hoppers and conduit, through a valve 120 located outside of the electrolytic cell and, ultimately to wash tank 48.

As will be evident, before the wash water is turned on to flush the copper powder out of hoppers 100 and discharge conduit 102, the electrolytic cell is discharged of its spent electrolyte through a port 122 in the bottom of the cell.

It should be noted that hoppers 100 are positioned beneath cathodes 103 but not beneath anodes 80. This arrangement is extremely important to prevent impurities trapped by anode bags 82 from dropping into the hoppers to contaminate the copper product. The purity of the copper product may be decreased by as much as 0.5% if this precaution is not observed.

Still another important aspect of the present invention is illustrated in FIGURES 5-9 of the drawings, in which is set forth a novel bus-bar assembly usable in connection with the electrolytic process described above. As shown in FIGURE 6, a plurality of female bus-bar leaves 200 are permanently mounted along each longitudinal edge 202 of an electrolytic vat 204, the upper longitudinal edges 206 of the female leaves being flush with the top edge 208 of the vat. Female bus-bar leaves 200 are mounted in parallelism with one another and are separated near their bottoms by copper spacer plates 210 (see FIGURE 7). Female leaves 200 and spacer plates 210 are secured to one another and to the longitudinal side walls 212 of the vat by means of bolts 214 which pass through the leaves, spacer bars and bores 216 in wall 212, the threaded ends 218 of the bolts passing outwardly into a countersunk slot 220 to permit the application to the end of the bolts of threaded nuts 222. To prevent warping of the outer bus-bar leaves, female leaves 200 and their respective spacer bars 210 are sandwiched between reinforcing plates 224 and 226, the former being adjacent side wall 212 of the vat. As shown

in FIGURE 6, a sufficient number of bolts 214 are provided along the length of female leaves 200 to assure a firm connection between the leaves and the side walls 212 of the vat.

Female bus-bar leaves 200 are provided along their length with a plurality of apertures 228 (see FIGURE 9) through which copper rods 230 pass (see FIGURE 7). Rods 230 pass also through corresponding apertures (not shown) in reinforcing plates 224 and 226, the ends of said rods projecting beyond the reinforcing plates as shown in FIGURE 7. End 232 of each rod 230 is threaded to receive a nut 234 which retains a spring 236 on that end of the rod. The other end 238 of each rod is pivotally connected at 240 to a lever 242 having a cam face 244. As shown in FIGURE 7, the cam face 244 of each of the levers 242 is maintained in engagement with reinforcement plate 226 through its pivotal connection 246 to two vertical support members 248, which may be seen more clearly in FIGURE 6. As is shown in FIGURE 7, wall 212 of vat 204 is recessed at 250 to receive the spring-carrying protruding ends 232 of rods 230.

FIGURE 9 shows an individual female bus-bar leaf 200, apertures 228 being provided for reception of rods 230 and apertures 252 being provided for receipt of bolts 214.

Secured to each of the longitudinal sides 254 of an electrode hanger frame 256 are a plurality of male bus-bar leaves 258, which are positioned in mating relationship to female bus-bar leaves 200, as illustrated in FIGURE 7. Male bus-bar leaves are separated from one another by copper spacer plates 260, as was the case with the separation of the female bus-bar leaves 200, and the male leaves and separator plates are secured to the longitudinal side 254 of hanger frame 256 by means of a plurality of electrode hanger rods 262 which are threaded at their ends to receive nuts 264 and 266 to secure the male leaves in place. Electrode hanger rods 262, which are preferably made of copper, extend beyond the longitudinal sides 254 of hanger frame 256 as at 268 and extend transversely across hanger frame 256 where they are received in the opposite longitudinal side member of the frame so that they will be supported at both ends (see FIGURES 5 and 6). Plate electrodes are mounted on hanger rods 262 in a conventional manner. [Note: The number of female leaves in FIGURE 5 has been reduced for purposes of illustration.]

The thickness of male bus-bar leaves 258 is slightly greater (i.e., $\frac{1}{16}$ ") than the separation between female bus-bar leaves 200 so that as the former are lowered between the latter, there will be a tight rubbing and surface cleansing action between the contact leaves of the male and female bus-bar assemblies. As will be apparent from the drawings, once the male bus-bar leaves 258 have been passed down and between female bus-bar leaves 200, more positive surface contact between the male and female leaves may be assured by proper rotation of cam lever 242, tension springs 236 permitting the adjustment of the cam lever locking position.

A detailed view of one of the male bus-bar leaves is shown in FIGURE 8. As illustrated therein, apertures 270 are longitudinally spaced near the upper edge of the male leaf to receive electrode hanger support rods 262, each leaf being provided along its lower edge with a plurality of cut-out portions 272 to permit the male leaf to ride over and beyond cam clamping rods 230. As will be apparent, as many cut-outs are provided as there are cam clamping rods 230.

The longitudinal ends 274 of male bus-bar leaves 258 extend beyond the longitudinal end 276 of hanger frame 256 to provide means to connect the bus-bar leaves to a power source in a conventional manner. As is shown in FIGURE 5, the leaves on one longitudinal edge of electrode mounting frame 256 are connected to the positive power source, the leaves on the other longitudinal

edge of the frame being connected to the negative power source. Electrodes supported from the former will serve as anodes; those supported from the latter will serve as cathodes.

The bus-bar assembly described above affords a positive, sure-grip electrode connection and practically eliminates poor electrical connections between the power source and the electrodes. In addition, this assembly makes removal of the electrodes from the vats for inspection, cleaning, etc., a simple and economical operation.

In the event that the ore which is used is substantially iron free, it may be necessary to utilize an alternative means to prevent excess polarization. Such a means is the automatic depolarizing circuit illustrated in FIGURE 10, which provides for successive alternative imposition of A.C. current and D.C. current on the electrolytic cell circuit. FIGURE 10 also illustrates a particularly efficacious manner of operating a pair of vats automatically for optimum efficiency while maintaining balanced temperature and conductivity control of both vats during operation.

The automatic depolarizing circuit in FIGURE 10 comprises a pair of A.C. to D.C. power converters 400 and 400' which have input terminals indicated at X, Y, Z and X', Y' and Z'. A three-phase, 60-cycle, 240-volt A.C. supply is provided at terminals 402, 404 and 406, and these terminals are connected to the contacts 401, 403 and 405 of a master control switch generally indicated at 407. The master control switch 407 is actuated by a coil 409 which is connected to a 220-240, 60-cycle A.C. supply source through a master "on-off" switch 411. The three-phase power from switch contacts 401, 403 and 405 passes through the line windings of reactors 408 and is connected to the contacts 411, 413, 415, 417, 419 and 421 of a three-pole double throw magnetic converter change-over switch indicated generally at 423. These same contacts are connected to converters 400 and 400' as indicated by the letters X, Y, Z and X', Y', Z'. This switch is controlled by a coil 425 which is energized from a 220-240-volt, 60-cycle single phase A.C. supply 427. The switch 423 is biased upwardly by a spring 423a and is pulled into its lower position when coil 425 is energized. The coil 425 of the magnetic converter change-over switch is energized through temperature and conductivity control devices presently to be described in greater detail.

The secondary coils 441 of the reactors 408 are connected across variable shunting resistances 443 and indicators 445. The indicators 445 may consist of light bulbs or volt meters and, in conjunction with the variable resistors 443, provide a means for balancing the current in the three supply lines and for preventing overload.

The power converters 400 and 400' provide 8-volts D.C. across the vat electrodes as will now be described in connection with the vat associated with converter No. 1.

D.C. supply to vat No. 1 busbars 200 and 258 is from converter 400 by way of bus-bar feeders 434 and 436. Connected across the D.C. supply is a high capacity filter condenser 438 utilized to filter out any ripple that may exit in the D.C. current from converter 400.

Alternating current input to the bus-bars is from an A.C. source 428 through transformer 442 by way of lead 444 to bus-bar 200 and by way of leads 446, 448 and 436 to bus-bar 258.

Connected in series with D.C. bus-bar feeder 434 is a heavy duty switch 450 including a movable wedge shaped contact 452 engageable with the split sections 454 and 456 of bus-bar 200. While this contact is shown as wedge shaped, it will be apparent that it could also be conical in form. These split sections are suitably clamped together by bolts 458 and 460 jointed to insulating plate 462. Secured to the upper edges of the bus-bar sections are a pair of Z-shaped brackets 464 and 466 bridged by a second insulating plate 468 against

which bears the lower end of a compression spring 470. Spring 470 surrounds actuating rod 472 carrying at its upper end wedge-shaped contact 452 and at its lower end magnetic core 474. The upper end of actuating rod 472 is threaded to receive a nut 476 and spring retainer 478, thus providing for adjustment of the tension on compression spring 470.

Surrounding core 474 is a D.C. solenoid holding coil 480 connected by way of lead 482 to terminal 484 of bus-bar 258. The other end of coil 480 is connected by way of lead 486 to one terminal 488 of a relay generally indicated at 490. The terminal 492 of switch 490 is connected by way of lead 494 to one side of the secondary winding of transformer 442.

The switch 490 includes a pair of movable contacts 496 and 498 separated by an insulating layer 500 and mounted for pivoting movement about a pivot carried by a standard 524. Movement of the movable arms of switch 490 toward electromagnet 516 is resisted by a coil spring 520 connected to a standard 524 and to the movable arms to bias the movable arms in a clockwise direction about the pivot 501. Movable contacts 496 and 498 are adapted to alternately engage stationary contact 504 and stationary contact 508. The stationary 504 is connected by way of lead 506 to the A.C. supply source 428 so that stationary contact 504 and movable contact 496 are operable to open and close the energizing circuit to the primary of transformer 442. Stationary contact 508 is connected by means of lead 510, bolt 458, bus-bar section 454, terminal 512 and bus-bar feeder 434 to the output of converter 400.

Switch 490 carries a holding magnet 514 or ferromagnetic disc adapted to be drawn against the terminal of electromagnet 516 which is energized from 120-volt A.C. supply terminals 517 through an adjustable thermo-time control device indicated generally at 519. This thermo control device comprises a single-pole, single throw switch 521 consisting of a switch arm 523 and bimetallic thermal element 525. A resistance heater element 527 is carried atop the bimetallic element 525 and has one end connected to a variable resistor 529. The variable tap on the variable resistor 529 is connected to the other power supply lead 517. It will be apparent that by varying the resistance 529, it is possible to vary the on-off time of the control switch 519. That is, as the element 527 heats and then cools, it causes the switch 519 to alternately open and close the circuit to the electromagnet 516 to thereby alternately switch the movable contacts 496 and 498 from one to the other position. The frequency of cycling of the switch 519 may be controlled by the variable resistor 529.

Referring now to the temperature and conductivity control devices for the coil 425 of the magnetic converter change-over switch 423, attention is directed to the upper right corner of FIGURE 10. A pair of vat control units 437 and 439 are provided in the form of commercially available A.C. Wheatstone bridge control circuits which are adapted to control the energization of a pair of relays 433 and 435 in response to two variable conditions. To this end, each Wheatstone bridge control unit has connected thereto a conductivity sensing unit 451 and a temperature sensing unit 453. As is known to those skilled in the art, this type of control circuit can be so designed as to actuate the relays 433 and 435 when either the conductivity or the temperature passes a limit which is dependent upon the other variable so that the control is a function of both temperature and conductivity. This is important since either temperature or conductivity control alone would actuate the controller before optimum conditions were achieved. Calibration controls 455 and 457 are provided for each variable (temperature and conductivity) on each control unit 437 and 439 and indicator lights 440 and 442 are provided to indicate when the controllers have been actuated.

The relay 433 in bridge controller 437 actuates arma-

ture 459 of a single pole double throw switch having an upper contact 461 and a lower contact 463. The armature 459 is normally in contact with the lower contact 463 until the relay 433 is energized to lift the armature into contact with the upper contact 461. This occurs when the hot spent electrolyte in vat No. 1 increases in conductivity and temperature and the sensing units 451 and 453 finally cause energization of relay 433 as the end point is reached. Adjustment for control of this function is provided by the calibration controls 455 and 457.

The bridge circuits 437 and 439 are shown only in such detail as is necessary to permit an understanding of their interaction and control functions, the details of such circuits being well known in the art. The bridge 437 is associated with vat No. 1 while the bridge 439 is associated with vat No. 2. Bridge 437 contains the usual transformer primary winding 600 with the indicator lamp 440 connected thereacross to indicate its energization. One side of this primary winding is connected by lead 602 to terminal 604 which, in turn, is connected to the A.C. supply 427. The other side of A.C. supply 427 is connected to terminal 606 and thence through a normally closed manual emergency switch 608 and lead 610 to the armature 459. The lower contact 463 is connected by lead 612 to terminal 614. The upper contact 461 is connected by lead 616 to terminal 618.

The other bridge 439 is substantially similar in construction and has an armature 620 associated with relay 435. Upper and lower contacts are provided for the armature 620 but only lower contact 622 is utilized. Lower contact 622 is connected by lead 624 to one terminal of the transformer primary 626 and the other side of this transformer primary is connected to a terminal 628. The indicator light 442 is connected across the transformer primary 626 to indicate its energization.

A second relay 642 is provided in bridge 439 and has its operating coil connected across the primary of the transformer 626 so as to be energized when that primary is energized. The relay 642 has a pair of armatures 644 and 646 associated with contacts 648 and 650. Armature 646 normally engages contact 650 when relay 642 is de-energized, while armature 644 engages contact 648 when the relay 642 is energized.

Terminal 614 on bridge 437 is connected by lead 630 to contact 650 of relay 642, while the corresponding armature 646 of that relay is connected by lead 652 to the upper side of the coil 425 of the change-over switch 423. The lower end of coil 425 is connected through a manual emergency switch 632 and lead 634 to the terminal 636 of the bridge 437. Terminal 636 is internally connected to terminal 604 which is itself connected to one terminal of the A.C. supply 427. The manual switch 632 is also connected to the armature 620 of relay 435 in bridge 439. Terminal 618 of bridge 437 is connected by lead 638 to terminal 628 of bridge 439. The transformer primary 600 in bridge 437 is connected by lead 640 to the upper side of the change-over switch coil 425. The armature 644 of relay 642 is connected by lead 654 to the armature 459 of relay 433 in bridge 437, while the contact 648 of relay 642 is connected by lead 656 to terminal 628 of bridge 439. This terminal is connected by lead 638 to terminal 618 of bridge 437.

The operation of the depolarizer control and converter change-over device is as follows: Closure of master "on-off" switch 411 energizes the holding coil 409 of the master switch 407 to provide a three-phase alternating current supply through reactors 408 and switch contacts 413, 417 and 421 to converter 400. This provides a supply of direct current to terminals 484 and 512 of bus bars 200 and 258. When the switch 490 is in the lower position by reason of energization of electromagnet 516 through the thermo control unit 519, the contacts 498 and 508 are closed to establish an energizing circuit for the holding coil 480 of the heavy duty switch 450 through

the following circuit: converter lead 436, terminal 484, lead 482, holding coil 480, lead 486, terminal 488, switch contact 498, stationary contact 508, lead 510, bolt 458, bus bar segment 454, terminal 512 and lead 434. This closes the heavy duty switch to supply D.C. from the converter 400 to vat No. 1.

After a period of time determined by the setting of the variable resistor 529 in the thermo control unit 519, the electromagnet 516 is deenergized, thereby opening contacts 498 and 508 to deenergize the holding coil 480 and thereby open the D.C. circuit just described. This circuit is physically opened by means of the spring 470 moving the rod 472 upwardly to move wedge 452 from between the two segments 454 and 456 of bus bar 200. At the same time that the switch 490 opens the contacts 498 and 508, it closes contacts 504 and 496. This establishes an alternating current depolarizing supply to the bus bars 200 and 258 through the following circuit: bus bar 200, bracket 466, lead 444, secondary of transformer 442, lead 446, lead 448, lead 436, terminal 484 and bus bar 258. The primary of the transformer 442 is energized through a circuit extending from alternating current supply 428 through the primary of the transformer and thence through lead 506 to contact 504, contact 496, terminal 492 and lead 494 back to the transformer primary. Alternating current is thus fed to vat No. 1 for a period of time determined by the thermo controller 519.

The alternate supply of direct current and alternating current to vat No. 1 continues until the temperature of this vat, in conjunction with the conductivity thereof, reaches such a value as sensed by the sensing devices 451 and 453 to cause the Wheatstone bridge controller 437 to actuate relay 433. This raises armature 459. It will be seen that prior to raising armature 459 the coil 425 of change-over switch 423 was energized through the following circuit: left terminal of A.C. source 427, terminals 604 and 636 of bridge 437, lead 634, switch 632, coil 425, lead 652, contact 650 and armature 646 of relay 642, lead 630, terminal 614, lead 612, contact 463 and armature 459 of relay 433, lead 610, switch 608 and terminal 606 to the right terminal of A.C. supply 427. During energization of coil 425 the change-over switch is pulled down against the bias of spring 423a and converter No. 1 is supplied with three phase power. When armature 459 is raised, as just described, the foregoing power circuit to coil 425 is broken, the coil is de-energized, and the change-over switch is pulled up by spring 423a to energize converter No. 2.

When armature 459 engages contact 461 several things happen. Power is supplied to the primary 626 of bridge 439 through a circuit extending as follows: Right terminal of A.C. supply 427, terminal 606, switch 608, lead 610, armature 459, contact 461, lead 616, terminal 618, lead 638, terminal 628, primary 626, lead 624, contact 622, armature 620, lead 634, terminal 636, terminal 604, and the left terminal of A.C. supply 427. At the same time that the transformer primary is energized, relay 642 is energized to cause armature 644 to engage contact 648 to provide a locking circuit about contact 461 and armature 459 to prevent de-energization of transformer primary 626 when relay 433 is de-energized; and armature 646 breaks its engagement with contact 650 to open the supply circuit to coil 425 so that, so long as transformer primary 626 is energized, coil 425 will not be energized when relay 433 is de-energized. Bridge 439 is now completely energized and in control of the process in the second vat. Alternating direct current and alternating current are supplied to vat No. 2 in precisely the same manner as just described in conjunction with vat No. 1.

When the electrolyte in vat No. 2 reaches its end point, as sensed by the sensing units 451 and 453 associated with bridge 439, the relay 435 is energized. Energization of this relay causes its armature 620 to raise and disengage from contact 622 thereby breaking the power

supply to transformer primary 626 and to relay 642. By the time that this has happened vat No. 1 has been emptied and recharged with pregnant electrolyte and relay 433 in bridge 437 is de-energized. The control circuit has thus automatically returned to its initial condition, coil 425 is again energized, and vat No. 1 is operating under the control of bridge 437. This cycle continues to be repeated automatically for optimum use of the equipment under completely automatically controlled operating conditions.

An example of the process of the present invention follows—

Ore content:

Soluble copper—4.0%; iron—4.0%; alumina—10.0%; lime—1.0%; silica—80.0%; remainder—moisture (percent by weight)

Ore size as dressed: Not more than 5% by weight coarser than $\frac{1}{4}$ " mesh; not more than 50% by weight coarser than 20 mesh (U.S. Standard Sieve).

Leaching solution (per approximately 1 ton of leaching solution):

Demineralized water—1816.9#

H₂SO₄ (93–95%) (S.G. 1.84)—182.3#

H₃PO₄ (orthophosphoric, 85%)—180.0 ml.

Versene Fe-3 specific (acidified to pH 4 with 5% H₂SO₄)—3.7#

Alumina (Al₂O₃)—1.0# (approx.)

Total approximate weight per ton of make-up Leaching solution—2003.9#

Total amount of Leaching solution used for one commercial unit batch (1,200 gals.)—2003.9#
×5=10019.5#

Weight ratio of leaching solution to ore: Approx. 1:1
Weight of ore used for one commercial unit batch: 10,000.0#

Leaching solution temperature: 130° F.

Method of agitation in leaching vat: Upward percolation

Leaching time: 1 hour

No. of anodes: 9

No. of cathodes: 8

Anode composition (by weight percent) [anode contains coating of lead peroxide]:

Pure soft lead—90

Pure antimony—10

Maximum impurity content:

Ag—.0004

Cu—.0009

Zn—.0005

As—.0003

Fe—.0002

Bi—.0014

Cathode composition: 99% pure rolled nickel sheet

Anode size: 30" wide, 39" long, $\frac{1}{2}$ " thick

Cathode size: 32" wide, 40" long, $\frac{1}{4}$ " thick

Electrode spacing: $2\frac{3}{4}$ "

Anode bags: Dynel-Vinyon, VN-753

Electrode connections: Parallel

Electrode starting voltage: 8.0 volts

Electrode voltage at end of cycle: 6.25 volts

Cathode current density at start of cycle (both sides of cathodes): approx. 250 amps./ft.²

Cathode current density at end of cycle (both sides of cathodes): approx. 500 amps./ft.²

Anode current density (throughout cycle): approx. 5% below cathode current density at any given time

Copper content of electrolyte:

40 gms./liter at start

15 gms./liter at end

Temperature of electrolyte:

Start: 15° C.

End: 55° C.

Circulation rate in electrolytic cell (upward): approx. 115 gals./min.

Electrodeposition time (for one commercial cell): 3.3 hours

Wash water temperature: 200° F.

No. of washes: 3

Washing time: $\frac{1}{2}$ hour each

Drying of copper powder: In hydrogen atmosphere at temperature gradually raised to 495° C.

The process and apparatus of the present invention provide many significant advantages. Not only is an extremely fine, pure copper powder obtained (purities of 99.5% and higher are readily obtainable, and 99.9% copper powder may be obtained with careful controls) by carrying out the process as above described but, in addition, a truly economical electrowinning process permitting continuous production of copper powder directly from copper ore in a single, continuous process is afforded. By means of this process, substantially 100% of the available copper in copper ore may be extracted, virtually eliminating waste and lowering the cost of the copper powder product. In addition, this process provides an extremely effective means for utilizing oxidized copper ores as raw materials without the necessity for pretreatment prior to leaching (aside from dressing operations which, by virtue of the present process, are greatly simplified) or for the use of blister or scrap copper.

One of the most important features of the present invention resides in the high temperature advantage resulting from the novel electrowinning process described above, an advantage not possessed by conventional electrolytic and leaching processes. More specifically, an important aspect of the present invention resides in the high temperature of the spent electrolyte removed from the electrolytic cell and the use of such high temperature solution to extract copper from another charge of dressed copper ore. The hot recycle leaching solution of the present invention affords a much greater and rapid penetration of the copper ores, thereby reducing long soaking time cycles. This high temperature solution thus makes possible a very rapid and efficient leaching cycle in comparison to known conventional methods since the latter do not have comparable temperature rises developed in the relatively slow electrowinning and Reguline deposition processes. In some cases, conventional methods even have to resort to added auxiliary equipment and sources of heat for use in connection with the leaching solution, which is quite costly and inefficient in comparison to the process of the present invention. The short leaching cycle permitted by the process of the present invention has a still further advantage, since the shorter the leaching period, the less likelihood there will be of extracting undesirably large quantities of impurities which, if present, could be extremely troublesome and result in possible solution discards.

Another important feature of the present invention is that the electrolytic process described results in the deposition of extremely pure dendritic crystals rather than granular copper which consists of cubic crystals. While the growth of dendritic crystals is difficult to control, the operating conditions heretofore set forth give crystals of high purity and of such surface perfection that oxidation is quite low despite the large surface area presented to the air by the mass of microcrystals. The problem in attaining such results was not only to discover the particular electrolytic conditions and electrolyte composition which would produce such crystals but to find means of preventing contamination by other metals and oxidation by the oxygen which is inevitably produced in the electrolytic reaction. These problems were solved by the process of the instant application by using materials such as Versene Fe-3 Specific and phosphoric acid to tie up the ferric ion which would otherwise contaminate the copper; by using electrodes with the right kind of electrochemical surface properties so that polarization effects will not interfere with the proper current flow for a given applied voltage; by using anodes which sweep out oxygen and chlorine from the electrolyte and which will not flake off or form any "anode mud" which could contaminate the copper

powder; by using cathodes which are resistant to attack and provide a proper surface for the deposition and growth of the dendritic microcrystals; by selecting the proper conditions of temperature, copper concentration, acidity and electrolyte circulation pattern to produce crystals of the desired structure, purity and size, etc.

But while best results are obtained by using the leaching and electrolytic processes in combination with one another (indeed, one of the critical aspects of the present invention involves the particular interrelationship between the various aspects of these processes, as set forth above), each of the portions of the overall process is itself patentably significant. Thus, the particular leaching process of the present invention may also effectively be utilized in connection with an electrolytic system utilizing a first-run low grade copper anode similar to those used in conventional electrolytic copper processes, rather than the particular lead-antimony anode described previously. Similarly, the particular electrolytic process of the present invention and the apparatus used therefor still retain many advantages when utilized in connection with a conventional leaching process.

As is apparent, all pipes, lines, valves, pumps, fittings, etc. should be chemical and corrosion proof.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by United States Letters Patent is:

1. A process for electrodepositing copper powder comprising: introducing an electrolyte into an electrolytic cell; said electrolyte being an H_2SO_4 -water solution containing dissolved copper; said electrolytic cell having cathodes formed of substantially pure nickel and anodes formed of a lead-antimony alloy; electrolyzing said cell to deposit copper powder from said electrolyte; said cell being maintained under the following conditions throughout said electrolysis:

(1) voltage between electrode pairs: at least approximately 6½ volts

(2) cathode current density per cathode side: at least approximately 125 amps./ft.²;

and removing said copper powder from said electrolyte and electrolytic cell.

2. A process as defined in claim 1 wherein the dissolved copper content of the electrolyte is at least approximately 15 grams/liter throughout the electrolysis.

3. A process as defined in claim 2 wherein the free acid content of the electrolyte is approximately 45–100 gms./liter throughout the electrolysis.

4. A process as defined in claim 3 wherein the maximum limits of the voltage between electrode pairs and of cathode current density per cathode side are respectively approximately 8 volts and 250 amps./ft.².

5. A process as defined in claim 3 wherein said anodes are composed of approximately 88–91% by weight of pure soft lead and 12–9% by weight of pure antimony.

6. A process as defined in claim 3 wherein the electrolyte contains at least approximately 25 grams of dissolved copper per liter of electrolyte at the beginning of the electrolysis cycle.

7. A process as defined in claim 6 wherein the temperature of said electrolyte is maintained at approximately 15–60° C. throughout said electrolysis.

8. A process as defined in claim 1 wherein, before the electrolysis is begun, said electrolyte contains about 100–500 mg. of ferrous iron per liter of electrolyte, the total amount of ferric and ferrous iron in said electrolyte not exceeding approximately 500 mg. per liter of electrolyte.

9. A process as defined in claim 8 wherein the recited range of ferrous and ferric iron is obtained by adding at least one compound selected from the group consisting of a tetrasodium salt of ethylenediaminetetraacetic acid and phosphoric acid to chelate any excess ferric iron, the amount of said tetrasodium salt if used being no greater than about 1.85 gms. per liter of electrolyte.

10. A process as defined in claim 1 wherein said cathodes are formed of approximately 99% pure rolled nickel sheet.

11. A process as defined in claim 10 wherein the maximum limits of impurities in said anodes are approximately (in weight percent): silver—.0004; copper—.0009; zinc—.0005; arsenic—.0003; iron—.0002; and bismuth—.0014.

12. A process as defined in claim 1 wherein said anodes are coated with lead peroxide prior to the commencement of the electrolysis.

13. A process as defined in claim 1 additionally comprising withdrawing spent electrolyte from said electrolytic cell; employing said spent electrolyte to form at least part of a leaching solution comprising an aqueous sulfate solution containing approximately 8–9% by weight of sulfuric acid; leaching copper-containing ore with said leaching solution to extract soluble copper therefrom; separating enriched leaching solution from the ore residue; and passing said enriched solution to said electrolytic cell to serve as the electrolyte.

14. A process as defined in claim 13 wherein said ore is of a size such that not more than approximately 5% of its weight is coarser than approximately ¼" mesh and not more than approximately 50% by weight is coarser than approximately 20 mesh.

15. A process as defined in claim 14 wherein said ore is leached for about 40 to 90 minutes.

16. A process as defined in claim 15 wherein the relative quantities by weight of leaching solution to ore are about 1:1 when the leachable copper content of the ore is less than approximately 4¾% by weight; about 1½:1 when the leachable copper content of the ore is between approximately 4¾–7½% by weight; and about 2:1 when the leachable copper content of the ore is greater than approximately 7½% by weight.

17. A process as defined in claim 16 wherein said water is substantially free of sodium chloride, calcium, iron and magnesium.

18. A process as defined in claim 15 wherein said ore is an oxidized copper ore.

19. A process as defined in claim 15 wherein said temperature of said leaching solution is approximately 110–130° F.

20. A process as defined in claim 1 wherein said anodes consist essentially of lead with approximately 9–12% by weight of antimony.

21. A process as defined in claim 20 wherein the electrolyte contains approximately 25–45 grams of dissolved copper per liter of electrolyte at the beginning of the electrolysis cycle.

22. A process as defined in claim 1 including the step of limiting free flow of electrolyte containing harmful impurities such as halogens towards the anodes so as to permit oxidizing action of said anodes to cause the electrolyte immediately adjacent said anodes to become more basic, thereby assisting in the liberation from the electrolyte as gases of such harmful impurities.

23. A process as defined in claim 1 wherein said electrolyte is recirculated at a rate of approximately ¼th of its volume per minute, the circulation of said electrolyte in the electrolytic cell being upward.

24. A process as defined in claim 1 additionally comprising withdrawing spent electrolyte from said electrolytic cell; employing said spent electrolyte to form at least part of a leaching solution comprising an aqueous sulfate solution containing approximately 1815 parts by weight of water and approximately 175–190 parts by weight of ap-

proximately 93-95% by weight sulfuric acid; leaching copper-containing ore with said leaching solution for about 40 to 90 minutes to extract soluble copper therefrom; said ore being of a size such that not more than approximately 5% of its weight is coarser than approximately $\frac{1}{4}$ " mesh and not more than approximately 50% by weight is coarser than approximately 20 mesh; the relative quantities by weight of leaching solution to ore being about 1:1 when the leachable copper content of the ore is less than approximately 4 $\frac{3}{4}$ % by weight, about 1 $\frac{1}{2}$:1 when the leachable copper content of the ore is between approximately 4 $\frac{3}{4}$ -7 $\frac{1}{2}$ % by weight, and about 2:1 when the leachable copper content of the ore is greater than approximately 7 $\frac{1}{2}$ % by weight; separating enriched leaching solution from the ore residue; and passing said enriched leaching solution to said electrolytic cell to serve as the electrolyte.

25. A process as defined in claim 1 wherein said anodes consist essentially of approximately 90% by weight of pure soft lead and approximately 10% by weight of pure antimony.

26. A process for electrodepositing copper powder comprising: introducing an electrolyte into an electrolytic cell; said electrolyte being an aqueous sulfate solution containing dissolved copper; electrolyzing said cell to deposit copper powder from said electrolyte and removing said copper powder from said electrolyte and electrolytic cell; the improvement comprising maintaining the cell under the following conditions throughout said electrolysis:

- (1) voltage between electrode pairs, at least approximately 6 $\frac{1}{4}$ volts;
- (2) cathode current density per cathode side, at least approximately 125 amps./ft.²;
- (3) free acid content of the electrolyte, approximately 45-100 gms./liter;
- (4) dissolved copper content of the electrolyte, at least approximately 15 gms./liter.

27. A process as defined in claim 26 wherein the electrolyte contains at least approximately 25 grams of dissolved copper per liter of electrolyte at the beginning of the electrolysis cycle.

28. A process for electrodepositing copper powder comprising introducing an electrolyte into an electrolytic cell; said electrolyte being an aqueous sulfate solution containing dissolved copper; said electrolytic cell having anodes composed of approximately 88-91% by weight of pure soft lead and 12-9% by weight of pure antimony; electrolyzing said cell to deposit copper powder from said electrolyte; and removing said copper powder from said electrolyte and electrolytic cell; the improvement comprising maintaining the cell under the following conditions throughout said electrolysis:

- (1) temperature of electrolyte, approximately 15-60° C.;
- (2) cathode current density per cathode side, at least approximately 125 amps./ft.²;
- (3) free acid content of the electrolyte, approximately 45-100 gms./liter;
- (4) dissolved copper content of the electrolyte, at least approximately 15 gms./liter.

29. A process for electrodepositing copper powder comprising introducing an electrolyte into an electrolytic cell; said electrolyte being an aqueous sulfate solution containing dissolved copper; said electrolytic cell having anodes composed of approximately 88-91% by weight of pure soft lead and 12-9% by weight of pure antimony and having cathodes composed of substantially pure nickel; electrolyzing said cell to deposit copper powder from said electrolyte; and removing said copper powder from said electrolyte and electrolytic cell; the improvement com-

prising maintaining the cell under the following conditions throughout said electrolysis:

- (1) temperature of electrolyte, approximately 15-60° C.;
- (2) cathode current density per cathode side, at least approximately 125 amps./ft.²;
- (3) free acid content of the electrolyte, approximately 45-100 gms./liter;
- (4) dissolved copper content of the electrolyte, at least approximately 15 gms./liter.

30. A process for electrodepositing copper powder comprising introducing an electrolyte into an electrolytic cell; said electrolyte being an aqueous sulfate solution containing dissolved copper; said electrolytic cell having cathodes composed substantially of pure nickel; electrolyzing said cell to deposit copper powder from said electrolyte; and removing said copper powder from said electrolyte and electrolytic cell; the improvement comprising maintaining the cell under the following conditions throughout said electrolysis:

- (1) temperature of electrolyte, approximately 15-60° C.;
- (2) cathode current density per cathode side, at least approximately 125 amps./ft.²;
- (3) free acid content of the electrolyte, approximately 45-100 gms./liter;
- (4) dissolved copper content of the electrolyte, at least approximately 15 gms./liter.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,262,870

July 26, 1966

George E. Harlan

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 54, for "elecrtto-" read -- electro- --;
column 9, line 58, after "antimony" insert -- content --;
column 12, line 23, for "leading" read -- leaching --; column
15, line 61, for "exit" read -- exist --; column 16, line 25,
for "tionary 504" read -- tionary contact 504 --.

Signed and sealed this 8th day of April 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents