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METHOD AND APPARATUS FOR ELECTRODEPOSITION

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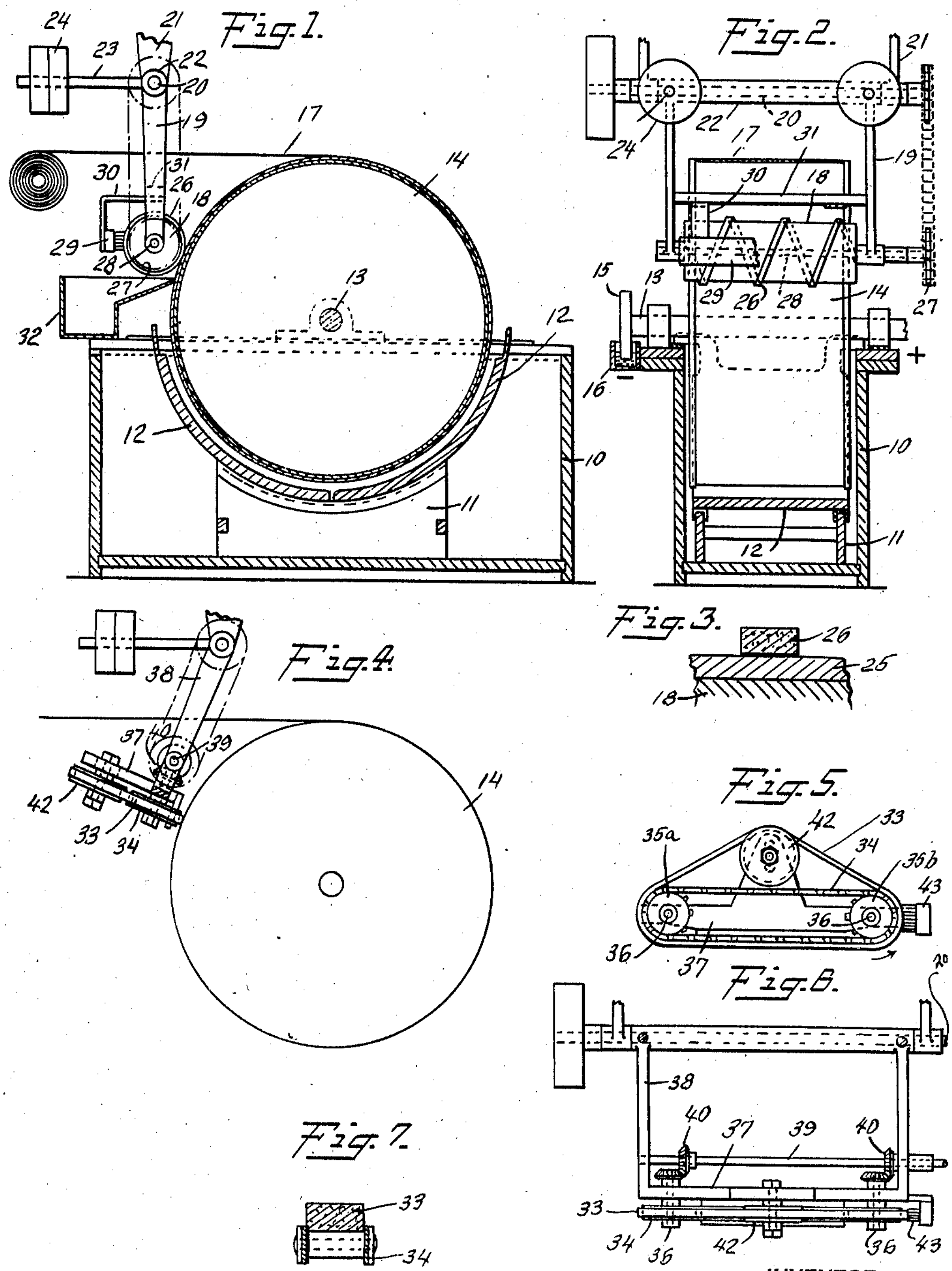


INVENTOR
Charles E. Yates
BY
Pennie, Davis, Marvin & Edmonds
ATTORNEYS

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## METHOD AND APPARATUS FOR ELECTRODEPOSITION

Charles E. Yates, Perth Amboy, N. J., assignor, by mesne assignments, to Anaconda Copper Mining Company, New York, N. Y., a corporation of Montana

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This invention relates to a method and apparatus for the continuous production of thin metallic sheets or foils by a process of electrodeposition involving the steps of plating metal on a traveling cathode surface and stripping it therefrom. More particularly, the invention is concerned with a novel method and mechanism for treating the cathode surface after stripping has been performed so that the surface is continuously renewed and may be used for long periods of time without replacement for the production of sheets or foils of high quality. The new method and apparatus may be used to especial advantage in connection with the production of thin copper foils and an embodiment of the invention in a form suitable for that purpose will accordingly be described to make clear the principles of the invention.

During a period of many years, numerous processes have been proposed, and in some instances patented, for the continuous electrolytic production of copper foils, but so far as I am aware, no process has so far been developed which is entirely satisfactory for the regular production of such foils on a commercial scale and, as a consequence, no thin copper foils are now on the market in commercial quantities. The proposed processes have had many objectionable features as, for example, they cannot be used to produce a foil of high quality and substantially uniform thickness, their output rate is low, they do not include a satisfactory cathode surface and method of maintaining it in proper condition, so that their operation is subject to frequent interruption, and they require much floor space. Many of the objectionable features of the prior processes are overcome in the process and apparatus described and claimed in application, Serial No. 507,126, filed January 7, 1931, in which I am a joint applicant with Solomon Levy and William M. Shakespeare, and the process and apparatus disclosed in that application can be used to produce first-class foils of uniform thickness and of different weights.

The fundamental problem in all continuous processes of electrodeposition, however, is the maintenance of the cathode surface in proper condition, and this problem is of the most serious character because of the profound effect on the foil produced of what are apparently minor defects in the cathode surface. This surface is subject to chemical changes, such as the formation of oxides, and it deteriorates rapidly because of the mechanical effect of the stripping, and changes of both kinds affect the foil adversely. As a consequence, many expedients have been proposed for keeping the cathode surface in satisfactory condition, but my experimentation with these prior proposals has shown that no completely satisfactory cathode surface and method of maintaining it have heretofore been developed.

The use of lead as a cathode surface is common in all electrolytic work by reason of its resistance to plating conditions, its cheapness, and the facility with which it may be handled and treated. Other metals, such as stainless steels and their alloys, silver, copper, tantalum, etc., have been suggested to replace the lead but some of these materials are available only in cast form and it has been found impossible to obtain castings of them which are free from cavities. Such of these materials as are available in sheet form present the difficulty of forming a satisfactory joint in connection with the production of a continuous surface. Sheet lead, however, can be obtained without cavities and a satisfactory joint can be made by burning.

Cathode surfaces made of lead, copper, silver, and possibly other metals can be used satisfactorily for a time by using stripping agents, such as iodine and mercury compounds, which are applied to the surface between stripping and deposition and, while these stripping agents alleviate the mechanical effect of stripping, they do not prevent corrosion of the cathode surface and their use is not satisfactory for continuous long-time operation. When lead is employed, for example, as the surface of a drum and the drum is freshly turned so as to provide a bright, clean, metallic surface, the operations of deposition and stripping without any treatment of the lead can be continued for several days, although as the operations proceed, stripping becomes more and more difficult and the mechanical effect of the stripping on the cathode surface increases. Also, pitting by corrosion is likely to take place and this increases the difficulty of stripping. Even if there is no pitting by corrosion, the difficulty of stripping increases because of the mechanical effect alone and while stripping may be continued for a considerably longer time if a stripping agent, such as an iodine compound, is employed, eventually pitting of the surface occurs.

The reason for pitting is not definitely known but it seems probable that it is due to the presence of minute particles of impurities such as lead oxide in the metal. Once pitting starts, the condition is aggravated by the mechanical effect of stripping and the result is that the deposited foil has holes in it and eventually the foil is torn in the stripping operation. When the condition of the surface has reached this point, the cathode has to be mechanically resurfaced and this operation represents a considerable item of expense, both for labor and for loss of time.

Numerous expedients have been suggested as a means for cleaning the surface mechanically just after stripping takes place and before the surface reenters the solution, but prior to the present invention, no means has been developed, so far as I am aware, which solves this problem.

In my experimental work, I have employed numerous cleaning devices as, for example, buffing wheels of soft material such as cotton or sheepskin but, although such devices appear to clean the surface properly, pitting takes place in the course of time. I have also attempted to use wire brushes for the purpose but have found them quite unsatisfactory in connection with continuous operation. A brush which is stiff enough to produce the desired cleaning effect causes irregularities in the cathode surface which are as objectionable as pitting, and fine wire brushes do not work well because, although they may not actually cut the lead, they soon produce grooves or corrugations which result in the production of defective foil.

Emery cloth, sand paper, and similar abrasives have been employed in ordinary electroplating for the preparation of the cathode surface where stripping is not involved but such abrasives are not satisfactory in connection with lead cathodes used in continuous processes for various reasons. All these abrasives soon become clogged with lead and cease to be effective and in addition they tend to leave irregularities in the lead surface which are equivalent in their action on the foil produced to natural pitting.

Another expedient that has been proposed is the use of a cathode surface of a rare metal, such as tantalum, but, while such metals have some advantages over lead by reason of their resistance to corrosion, they require cleaning to remove oxides and their cost prohibits their regular use.

After much experimentation in this field, I have found that the difficulties above pointed out in the continuous electrolytic production of foils on a commercial scale can be overcome by employing a cathode surface of lead and continuously renewing this surface between stripping and deposition so that the deposit always takes place on a smooth, bright, clean metallic surface. In producing such a surface, I remove the matter which accumulates on the lead during deposition, including the film of oxide, and a thin film of the metal itself, and I carry on the operation of renewing the surface by means which do not score or produce irregularities.

The mechanism which I employ for maintaining the surface of the cathode in proper condition includes an element having a working surface which performs the two functions of abrading and burnishing or smoothing the cathode surface on which it operates and this element is so constructed that the working surface does not become clogged with the material removed from the cathode even after continuous operation over a period of months. The working surface of the element consists of finely divided abrasive particles supported or embedded in a resilient mounting and, for this purpose, the particles may be incorporated in a mounting of a vulcanized rubber compound. The particles employed may be of various abrasive materials, for example, silicon carbide, and these particles are of approximately 200 mesh and graded so that they are of the same size in all directions and not long and thin as might be the case if they were not subjected to the special grading operation. The rubber compound employed is one which is fairly flexible and soft but without tendency to become gummy or to smear in operation. Even though vulcanized, the compound is not brittle. While varying proportions of rubber and abrasive may be employed, as, for example, about 20 percent by weight of the abrasive to 80 percent by weight of the rubber compound, the proportions employed must be such that the compound is present in a preponderating or major amount while the abrasive is present in a minor amount. By employing such proportions, a material is produced which has a working surface in which there is enough of the rubber compound to perform a substantial smoothing or polishing action. In this respect, the operating element is distinguished from abrasive wheels and other articles of that type in which rubber is employed merely as a binder for the abrasive particles and only a relatively small proportion of rubber compound is employed and it performs no substantial smoothing action.

The operating element is of the traveling type and it may take various forms, such as that of a cylindrical drum, a helical strip wound on a cylindrical surface, or a traveling belt. The element is carried in a floating mounting biased toward the cathode surface and bearing against the latter with the desired pressure. When the element is in the form of a drum or a strip wound about a cylindrical surface, the element is mounted with its axis parallel to that of the cathode surface and it rotates in a direction opposite to the direction of movement of the cathode surface. When an element of the belt type is used, it is preferably mounted so that it moves parallel to the axis of rotation of the cathode surface.

In any form of the element, it is driven at a surface speed substantially higher than the speed of the cathode surface, and in its movement, the element removes the film of oxide on the cathode surface and a thin film of metal, this function being performed by the abrasive particles. The rubber mounting of those particles contacting with the cathode surface smooths and burnishes the latter so that the formation of irregularities is substantially prevented. The material removed from the cathode surface is in the form of a light powder and with the abrasive particles distributed through the soft rubber compound, there is no tendency, as in the ordinary abrasive wheel, for the material thus removed to collect between the particles and impair the abrading action.

The self-cleaning action of the element probably results from the resilience of the mounting which is pressed away from the particles by contact with the cathode and when free of the cathode, springs back and forces the removed material away from the abrasive particles. In any event, clogging of the working surface does not take place and the material removed from the cathode surface remains on the operating surface of the element in powdery form and may be readily removed therefrom, for example, by a light brush. If any of this powder adheres to the cathode surface and metal is plated thereover, a pinhole develops in the deposit. For this reason, it is advantageous to employ an operating element in the form of a drum or a strip wound on a cylindrical surface and run the drum or cylindrical element in a direction counter to the direction of movement of the cathode surface, since with this arrangement, any powder which is thrown free of the element and adheres to the cathode surface, advances again to the point of contact of the element and the cathode surface and cannot pass beyond the point of contact and be carried into the plating tank.

For a better understanding of the invention, reference may be had to the accompanying drawing, in which

Fig. 1 is a view in vertical cross-section through one form of apparatus suitable for carrying on the new method;

Fig. 2 is a sectional view taken at right angles to Fig. 1 with certain of the parts shown in elevation;

Fig. 3 is a cross-sectional view through a portion of the operating element illustrated in Fig. 2;

Fig. 4 is a view in side elevation of a modified form of apparatus, the drum being illustrated conventionally;

Fig. 5 is a plan view of a portion of the apparatus shown in Fig. 4;

Fig. 6 is a view of the apparatus illustrated in Fig. 4 in end elevation with parts removed; and

Fig. 7 is a sectional view through a portion of the apparatus shown in Figs. 4 to 6, inclusive.

In the drawing, the apparatus is shown as including an electrolytic tank 10 of any suitable or convenient construction containing a support 11 for curved anodes 12. Mounted on the shaft 13 supported, for example, on the top of the tank is a cathode drum 14, this drum being so supported that a portion of it dips beneath the level of the solution within the tank. The drum has a surface of lead which is connected to the negative side of the source of energy as, for example, by having its shaft provided with a disc 15 which dips into a mercury bath 16 connected to the negative supply line.

A drum which I have found suitable for use in the production of copper foils comprises a copper framework which includes a pair of wheels, one at each end of the drum, heavy sheet copper being bolted on the outside of the wheels to close the drum structure. A lead plate preferably made of lead with a small amount of antimony, such as from 4% to 6%, is then bent to proper shape and slipped endwise over the drum structure, the joint between the meeting edges of the lead plate being then filled in with lead by the usual burning operations. The plate is preferably a rolled plate about one inch thick free from oxides and other foreign matter. After the plate has been mounted on the drum and the joint closed, the surface is turned down to a true cylinder by means of a lathe.

In the operation of the device, copper is deposited on that portion of the drum surface which is immersed in the solution and the drum rotates slowly so as to build up a deposit of the desired thickness. As the drum continues its rotation, the deposit is stripped off at a point near the top and the foil 17 is then rolled up in any convenient manner. The speed of rotation of the drum depends on the current and various other factors.

In order to renew the plating surface on the drum after the stripping operation, I provide a drum 18 mounted on a shaft supported in the ends of arms 19 pivotally mounted in any convenient manner as, for example, on a driven shaft 20 carried in fixed bearings in hangers 21, and driven by any suitable means. In the construction shown, the arms 19 are connected to a sleeve 22 through which the shaft 20 extends and attached to the sleeve and extending in a generally horizontal direction are arms 23 carrying weights 24. These weights tend to swing the arms 19 in a counterclockwise direction. The supporting structure for the drum 18 is so placed that the drum bears against the surface of the cathode drum preferably at a point not far removed from the place where the moving surface of the cathode drum enters the solution.

The drum 18 may conveniently take the form of a metallic tube or core of suitable dimensions, on the outer surface of which is secured a covering 25 of soft rubber. The abrasive element 26 is secured to the surface of the rubber covering by cement and, in the construction illustrated, the element has the form of a strip which is wound helically about the drum.

The cathode drum which I have found satisfactory in service has a substantial diameter such as 66 inches and with this, I employ a cleaning element comprising a drum 18 approximately 5½ inches in diameter with the strip 26 laid helically with a pitch of 8 inches. The rubber coating on the cleaning drum may have a thickness of ½ inch and the strip may have a width of ¾ inch and a depth of ½ inch. With the cathode drum operating at a surface speed of 9 inches per minute, the cleaning drum 18 is driven at a relatively higher surface speed, for example 3250 inches per minute, and against the direction of the drum surface, and the weights employed may, for example, be 80 pounds. The cleaning drum can be driven in any convenient manner as, for example, by means of a sprocket wheel 27 on the end of the shaft 28, the wheel being driven by a chain from a wheel on driven shaft 20.

The use of the abrading element 26 in the form of a strip wound helically about a drum is not essential but provides a convenient and economical method for using the abrasive material. If desired, however, the entire surface of the drum may be covered by the abrasive compound. When a helical strip is employed, it must be prevented from swaying and, accordingly, it is best to form the strip of oblong section and apply it with its longer side against the rubber cushion. After the drum is provided with the abrasive element, it is turned down so as to have a true cylindrical surface so that the drum will run smoothly in contact with the cathode surface and not be thrown clear by eccentricities.

In the operation of the device as described, the abrasive material on the surface of the drum not only removes the oxides and other foreign matter which may have collected on the cathode surface but also removes a thin film of metal, so that the cathode presents a bright, clean, metallic surface for each deposition of metal upon it. By reason of this removal of a thin film of metal from the cathode prior to each deposit upon it, any impurities in the metal which in the course of time would result in pitting are removed, and thus the cause of pitting is eliminated before a condition which leads to pitting has a chance to become established. The abrasive particles distributed through the rubber compound serve to remove the foreign matter and the thin film of lead and the rubber mounting appears to properly limit the abrading action of the particles and to effect a smoothing or burnishing action which tends to counteract the tendency of the particles to produce an objectionable grain effect.

The abrasive surface or strip on the drum 18 must be kept clean to be effective, and, for this purpose, I use a brush 29 which may be conveniently mounted in supports 30 attached to the cross bar 31 extending between the arms 19. This brush merely serves to remove fine powder loosely resting on the surface of the abrasive element. Beneath the drum 18 and the brush is a receptacle 32 in which the foreign matter and lead powder removed from the cathode surface are collected.

While the apparatus described has proven highly satisfactory, I have found that the modified construction illustrated in Figures 4 to 7, inclusive, also gives satisfactory results. In the modified form of apparatus, the abrasive element is a belt 33 of the material previously described, mounted to travel over the outside of a chain 34 which is led around sprocket wheels 35*a*, 35*b*, mounted on shaft 36 supported in bearings in a cross bar 37 extending between arms 38. The arms are pivotally mounted and weighted, the constructon being generally similar to that illustrated in Fig. 1. The shafts on which the sprocket wheels are mounted are driven from a shaft 39 by bevel gearing generally designated 40, the shaft 39 being driven from shaft 20 in any convenient manner, as by a chain. Throughout a portion of its length, the abrasive belt is out of contact with the chain and passes over an idler pulley 42 adjustably mounted in an extension from the cross bar 37, this pulley permitting the belt to be kept taut at all times. The arms 38 are mounted in such position that the stretch of the belt in contact with the chain is forced against the surface of the cathode drum 14 and the belt is driven across the surface at a relatively high speed. The belt is continuously cleaned by means of a brush 43 attached to the cross bar 37 and bearing on the belt at a point just beyond the contact of the belt with the cathode drum.

With the modified construction shown, it will be apparent that the belt of rubber-abrasive compound is supported firmly in contact with the surface of the cathode drum by means of the chain and the abrasive material has the effect previously described of removing foreign matter from the surface of the drum and also of removing a thin film of the metal. Since the travel of the abrasive belt is across the direction of movement of the cathode surface and the belt and the cathode move at different surface speeds, the abrasive particles in the belt have little or no cumulative effect.

Instead of using a belt of rubber-abrasive material mounted so as to extend across the direction of movement of the surface of the drum and driven by suitable means, I may employ an endless chain or belt on which blocks of the abrasive material are mounted. For this purpose, it may be convenient to secure each rubber block to a metal base which can then be attached to the belt or chain in any suitable manner. When such a belt or chain is employed, it is trained about sprocket wheels on a floating mounting and guide means may be provided for supporting that stretch of the belt carrying the blocks which contact with the cathode surface. Such a support serves the same purpose as the chain used in connection with a belt made entirely of the abrasive material. When the blocks are employed, they are preferably bevelled along one side so that injury to the blocks and the cathode surface will be avoided when the blocks come into contact with it.

With the new method of continuous production of foils electrolytically, the cathode surface is not only continuously kept clean but also continuously renewed, a new metallic surface being exposed to the plating solution on each revolution of the drum. At the same time, the surface of the drum is continuously polished and burnished so that no objectionable grain is obtained.

What I claim:

1. In apparatus for electrodeposition, the combination of a rotating cathode drum on which metal is continuously deposited and from which the deposit is continuously stripped, and means for treating the drum surface between stripping and deposition on the surface, said means including a mounting, a traveling element in the mounting having a working surface made up of abrasive particles embedded in relatively soft flexible rubber, said surface including a proportion of rubber sufficient to effect a substantial smoothing action and means for driving the element at an angle to the direction of movement of the cathode surface and at a surface speed higher than that of the cathode.

2. In apparatus for electrodeposition, the combination of a rotating cathode drum on which metal is continuously deposited and from which the deposit is continuously stripped, and means for treating the drum surface between stripping and deposition on the surface, said means including a mounting, a drum in said mounting carrying an element made up of abrasive material embedded in relatively soft flexible rubber, said element having sufficient rubber in its working surface to effect a substantial smoothing action means maintaining the drum with said surface of the element in contact with the cathode drum, and means for rotating the drum in said mounting at a higher surface speed than said cathode drum.

3. A method of producing a metallic sheet by electrodeposition which comprises depositing metal on a polished metallic surface, stripping the deposit from the surface, and thereafter abrading the surface, to prepare it for the reception of another deposit, by means of an element moving relative to said surface and composed of fine abrasive particles of a substantially uniform grading distributed in a relatively minor amount through a major proportion of a soft rubber compound, the rubber compound serving to polish the abraded surface.

4. A method of producing a metallic sheet by electrodeposition which comprises depositing metal on a polished metallic surface, stripping the deposit from the surface, thereafter abrading the surface to prepare it for the reception of another deposit, by means of an element moving relatively to said surface and composed of fine abrasive particles of a substantially uniform grading distributed in a relatively minor amount through a major proportion of a soft rubber compound, the rubber compound serving to polish the abraded surface, and continuously cleaning the working surface of the element.

5. A method of producing a metallic sheet by electrodeposition which comprises moving a cathode surface of polished lead alternately into and out of the solution in an electrolytic tank, depositing metal upon said surface during its immersion, stripping off the deposit, and continuously abrading the surface to prepare it for an-

other deposit by means of an element moving relatively to said surface and composed of fine abrasive particles of a substantially uniform grading distributed in a relatively minor amount through a major proportion of a soft rubber compound, the rubber compound serving to polish the abraded surface.

6. Apparatus for the electrolytic production of sheet metal, which comprises an electrolytic tank, a cathode surface movable alternately into and out of the solution in the tank, means for depositing metal on the surface while it is immersed, said deposit being stripped from the surface when the latter is out of the solution, and means for abrading the surface from which the deposit has been stripped to prepare said surface for another deposit, said means including an operating element consisting of fine abrasive particles of substantially uniform grading distributed in a minor amount through a major proportion of a soft rubber compound, said compound serving to polish the abraded surface.

7. Apparatus for the electrolytic production of sheet metal, which comprises an electrolytic tank, a cathode surface movable alternately into and out of the solution in the tank, means for depositing metal on the surface while it is immersed, said deposit being stripped from the surface when the latter is out of the solution, and means for abrading the surface from which the deposit has been stripped to prepare said surface for another deposit, said means including an operating element consisting of fine abrasive particles of substantially uniform grading distributed in a minor amount through a major proportion of a soft rubber compound, said compound serving to polish the abraded surface, and means for cleaning the working surface of said element.

8. Apparatus for electrodeposition, which comprises a polished metallic cathode surface, on which metal is deposited and from which the deposit is stripped, and means for abrading said surface to prepare it for the reception of a deposit, said means including a working element consisting of fine abrasive particles of substantially uniform grading distributed in a minor amount through a major proportion of a soft rubber compound, said compound serving to polish the abraded surface, and means for moving said working element relative to said cathode surface.

9. Apparatus for electrodeposition, which comprises the combination of a moving cathode surface on which metal is deposited and from which the deposit is stripped, said surface being polished, and means for abrading said surface to prepare it for another deposit, said means comprising an operating element made up of fine abrasive particles of substantially uniform grading distributed in a minor amount through a major proportion of a soft rubber compound, said compound serving to polish the abraded surface, means for moving said element relative to the cathode surface, and means for cleaning the surface of said element.

10. In apparatus for electrodeposition, the combination of a moving cathode surface of polished metal on which metal is deposited and from which the deposit is stripped, and means for abrading said surface to prepare it for another deposit, said means comprising a traveling element made up of fine abrasive particles of substantially uniform grading homogeneously distributed in a minor amount through a major proportion of a soft flexible rubber compound, said rubber compound serving to polish the abraded surface, and means for driving said element in contact with said cathode surface.

11. In apparatus for electrodeposition, the combination of a moving cathode surface of polished metal on which metal is deposited and from which the deposit is stripped, and means for abrading said surface to prepare it for another deposit, said means comprising a drum, a working element on the surface of said drum consisting of fine graded abrasive particles distributed in a minor amount through a major proportion of a soft flexible rubber compound, said rubber compound polishing the abraded surface, and means for rotating said drum while said working element is in contact with the cathode surface.

12. In apparatus for electrodeposition, the combination of a moving cathode surface of polished metal on which metal is deposited and from which the deposit is stripped, and means for abrading said surface to prepare it for another deposit, said means comprising a drum, a working element on the surface of said drum consisting of fine graded abrasive particles distributed in a minor amount through a major proportion of a soft flexible rubber compound, said rubber compound polishing the abraded surface, said element being in the form of a strip wound helically about said drum, and means for rotating said drum while the working element thereon is in contact with the cathode surface.

13. In apparatus for electrodeposition, the combination of a moving cathode surface of polished metal on which metal is deposited and from which the deposit is stripped, and means for abrading said surface to prepare it for another deposit, said means comprising a traveling belt having a working surface made up of fine graded abrasive particles homogeneously distributed in a minor amount through a major proportion of a soft rubber compound, said compound acting to polish the abraded surface, and means for driving said belt with its working surface in contact with the cathode surface.

14. In the art of electrochemistry, an element for treating a surface to prepare it for reception of a deposit, said element comprising a soft rubber compound in preponderating amount and a minor proportion of fine abrasive particles of substantially uniform grading homogeneously distributed through said compound, said compound having a polishing action on the surface abraded by said particles, and means for moving said element in contact with and relative to the surface to be treated.

15. In apparatus for electrodeposition, the combination of a rotating drum cathode having a surface of polished lead on which metal is deposited and from which it is stripped, and means acting on said surface after the deposit has been stripped to prepare the surface for reception of another deposit, said means comprising a yieldable polishing element made up of a minor proportion of abrasive particles of substantially uniform size and a major proportion of a soft rubber compound through which said particles are distributed, said compound acting to polish the surface abraded by said particles, and means for moving said element in contact with and relative to said polished lead cathode surface.

CHARLES E. YATES.