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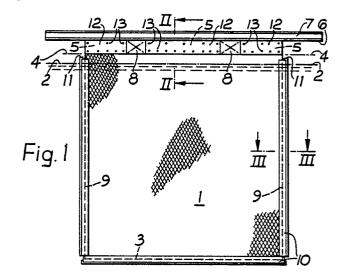
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- (54) Matrix-plates for the production of detachable electrodeposits, and electrodeposition method and product.
- The invention also relates to any process of electrodeposition of such as a metrix-plate, and to the products of such process.



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### MATRIX-PLATES FOR THE PRODUCTION OF DETACHABLE ELECTRODEPOSITS, AND ELECTRODEPOSI-TION METHOD AND PRODUCT

This invention relates to a matrix-plate for the electrolytic deposition of metal and/or of a metalrich compound such as a metal-oxide, to a method of electrolytic deposition of metals and/or of metalrich compounds, and to the product produced by such method.

1

Matrix-plates are electrodes used in the production of detachable electrodeposits of metals and/ or of metal-rich compounds such as oxides. The matrix-plate may be anodic (as, e.g., in the production of manganese), or it may be cathodic -(as in electrolytic refining -"E R" -and in electrowinning -"E W" -of such metals as, e.g., copper, nickel, cobalt and zinc), or it may act as a bipolar or intermediate electrode in special processes. The principle of this invention applies irrespective of the matrix-plate's polarity, and the invention is applicable (but not necessarily confined) to any of the processes cited above by way of examples. It is especially relevant to ER and EW of (e.g.) copper, nickel, cobalt and zinc, where the matrix-plates serve as cathodes. Important advantages accrue from the application of this invention to ER and E W -more especially of copper: it is with special reference thereto that the invention is hereinafter described in detail; matrix-plates used in copper E R and E W are also referred to as "(mother)blanks".

These blanks are generally of rectangular shape, and metal (here: Cu) is electrodeposited onto both faces of the plate. The electrodeposit would not be readily detachable if it enveloped the matrix-plate: envelopment is prevented by means of so-called "edge-protectors" which are fitted to the blank's vertical side-edges, and, in some cases, also to its horizontal bottom-edge, to keep these edges free from electrodeposition, and thus to enable the electrodeposited metal to be detached, i.e. stripped, from both faces of the blank.

ER and EW of copper has until recently always employed two stages of electrodeposition: in the first stage, mother-blanks are used to receive a deposit of (e.g.) 1mm thickness, which is stripped from the blank, and then is flattened and trimmed; conductor-straps are then attached (usually by rivetting) to the 1mm thick sheet, which then serves as the cathode -the so-called "starter-sheet" in the second stage of electrolysis, to be built up to "commercial" thickness. This two-stage method, utilising starter-sheets, is still employed in the great majority of Cu Refineries.

More recently, however, methods have been developed to produce ER and EW copper by single-stage electrodeposition, dispensing with starter-sheets, and using so-called "permanent cathodes" as matrix-plates, which receive detachable deposits of upwards of 6mm thickness on each face to yield "commercial" copper cathodes weighing some 45-50kg each, from single-stage electrolysis. Moreover, the process lends itself to be extensively mechanised or automated, thus reducing the element of human error, and being specially attractive where tankhouse-labour is at a premium. The patented "ISA PROCESS" (developed by Copper Refineries Pty. Ltd. 'CRL' at Townsville, Queensland, Australia) uses such permanent cathodes, the design of which is protected by U.K. Patent Applications Nos 2040311 and 822241.

For starter-sheet production, the mother-blanks originally were made of copper, needing careful surface-passivation prior to each electrodepositioncycle so as to ensure detachability of the deposited starter-sheet; moreover, the copper blank is subject to corrosion at the air/acid-electrolyte interface: in practice. it is not feasible to control and maintain the liquid-level in each cell with the accuracy needed to prevent such interfacial corrosion. Efficient edge-protection (including of the horizontal bottomedge) is essential. Copper blanks usually are 4-5mm thick. Their useful life is somewhat limited but this and their aforementioned other disadvantages are outweighed to some extent by relatively low first-cost, together with on-site salvage of wornout blanks which are just returned to the Smelter. For these reasons, but more especially because of the high cost of re-equipping with starter-sheet blanks made of titanium or stainless steel, many Tankhouses continue to use copper blanks.

Several important Refineries, and especially most of those built since the late 1950ies, now employ titanium blanks for starter-sheet production. Titanium does not need surface-repassivation for each electrodeposition-cycle, nor is it necessary to fit bottom-edge-protectors, nor is there any corrosion at the air to electrolyte interface. Titanium blanks usually are 3mm-3.2mm thick.

Stainless steel blanks are a less expensive alternative to Ti blanks, but need surface-passivation before each deposition-cycle, as well as efficient bottom-edge protection. These disadvantages generally outweigh the lower first-cost of stainless steel vs. titanium for starter-sheet blanks -the average Tankhouse needs (e.g.) 2,000 -4,000 such blanks.

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But where "permanent cathode" matrices are concerned, the average requirement is of the order of 40-50,000 blanks: although stainless-steel plates are usually 4mm thick while 3mm is adequate for titanium, the investment is very significantly lower for S/S: but, even so, it is still too high for the majority of operators who would otherwise have opted for single-stage electrodeposition to dispense with starter-sheets. Automation of the passivation-process also requires substantial investment: when labour-costs are high, there is little incentive to abandon starter-sheet production in favour of a labour-intensive operation requiring the purchase of S/S permanent cathodes. Such a purchase would be more justifiable in installations where there is a modern lay-out which lends itself to further automation without major additional investment.

The first-cost of a metal plate (such as a matrix-plate or mother-blank) all other things being equal is determined by its weight: for any given size, this is a function of the plate's thickness. In the present application, the thickness is subject to one or more of the following parameters, viz. :-(a) the plate must have adequate mechanical strength and must be rigid enough to resist deformation; (b) it may be necessary for the thickness to include allowance(s) for mechanical abrasion and/or corrosion (e.g., at the air:liquid interface, as already discussed); moreover: (c) permanent cathodes may be subjected to somewhat greater stresses during mechanised handling -but their thickness may result in excessive overall weight when "commercial" thickness of copper has been deposited: in such a case, it may be preferable to reduce the surface area of such matrix-plates rather than to increase their thickness.

Titanium mother-blanks for Cu starter-sheets generally are 3mm-3.2mm thick, which gives adequate rigidity to plates of up to some 1.5m² surface area/face. When used with efficient edge-protectors (such as the "EDGEWISE'(Trade Mark) system described in UK Patent No 2080829), sticky deposits are all but eliminated, so that no special abrasion allowance is necessary.

Stainless-steel "permanent cathode" matrixplates may be from 3.25mm up to 4.76mm (3/16") thick, made of AISI St. 304 or 304L, though AISI St. 316 and 316L have also been used, but are more expensive.

Flatness of matrix-plates is very important, because the inter-electrode distance in the cells is small. Bowed cathodes at best result in uneven thickness of electrodeposits, and -at worst may

cause short-circuits. Rigid edge-protectors such as are used in the "EDGEWISE' (Trade Mark) system (B.P 2080829) help to eliminate short-circuits, but cannot straighten a badly-bowed matrix-plate.

The alternative ways of modernisation and of increasing efficiency in copper cathode production in ER and EW operations may thus be summarised as follows -and all involve investment on a scale which many operators find excessive, viz.:-

- (1) Building a new tankhouse incorporating such as the ISA PROCESS or ONAHAMA system. Though a number of feasibility studies usually are in progress, there are very few potential investors prepared to proceed.
- (2) Modification of existing facilities to enable permanent S/S cathodes to be passivated for each cycle by other than labour-intensive methods.
- (3) Purchasing Ti permanent cathodes which do not need cyclic repassivation.
- (4) Continuing with starter-sheet production, but replacing existing Cu blanks with Ti blanks.

The object of the invention is to enable any of these alternatives to be effected at significantly reduced first-cost, the invention opening up additional advantageous possibilities as described hereinafter.

According to a first aspect of the invention, there is provided a mother-blank matrix-plate to receive upon its surface electrolytically-deposited layers of metal and/or of a metal-rich compound such as a metal-oxide which are readily detachable from that surface, by virtue of the said mother-blank matrix-plate during its manufacture having undergone a process of cold-working of such intensity as to significantly reduce the grain or crystal size right through the thickness of the said mother-blank matrix-plate thereby evidencing the absorption of free energy in its crystal-structure.

According to a second aspect of the invention, there is provided any process for the electrodeposition of readily detachable layers of metal or of a compound rich in metal such as an oxide, and employing a mother-blank matrix-plate as described above.

According to a third aspect of the invention, there is provided a product resulting from any process as defined above.

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The structure of a metal plate is changed by intensive cold-working so as to reduce its grainsize throughout its thickness, causing what may be termed penetrative (rather than superficial) absorption of free energy, thereby to facilitate the ready detachability of metal and/or metal-rich compound -(in accordance with the third aspect of the invention) electrolytically deposited upon the plate's surface (in accordance with the second aspect of the invention), and thus wholly eliminating or at least substantially reducing the frequency, and the attendant cost, of any preparatory treatment which would otherwise have been necessary to ensure that ready detachability of electrodeposits from that surface. The structural changes resulting from the aforementioned intensive cold working will inevitably increase the rigidity of the metallic plate, and thus -all other things being equal -its thickness, and hence both its weight and its initial cost may be reduced from the levels which, in the absence of such intensive cold-working aforesaid, would have been necessary to provide a plate of the required rigidity.

In detail, by employing the features of the invention, first-cost savings of more than 40% are achieved when comparing the cost of (for example) 4mm thick, plain, as-rolled, bright-annealed stainless steel plate AISI St.304, with that of 1.2mm thick rigidized sheet of the same material and specification. Rigidized sheet also yields a slightly larger effective surface-area for the same overall dimensions: depending on the rigidizing pattern, the area-increase ranges between 7% and 10%. First-cost savings for titanium are even greater: comparing, e g , 3mm thick plain, as-rolled Tisheet with 1.2mm rigidized sheet, the saving amounts to some 45%, and for 1mm thick rigidized sheet the saving compared to 3mm plain material is 50%. All of these comparative figures relate only to the so-called "blade" of the blank: the cost of carrier-/busbars and of edge-protectors, and of fitting all of these, is additional, and is constant irrespective of the thickness of the blade.

Conventional, i.e. non-rigidized, titanium blanks have, as mentioned previously, the important advantage over those made of copper or (non-rigidized) stainless steel, of not needing repassivation treatment for each deposition-cycle, nor bottomedge protection. Rigidized titanium is no different in that respect -but it has been found that rigidized bright-annealed or annealed + pickled stainless steel AISI St.304 blanks -unlike those of non rigidized sheet -do not require repassivation for each cycle. This fact very greatly enhances the cost-

advantage of stainless steel over titanium, and is especially important where "permanent cathodes" are concerned, as, for example, in the ISA PROCESS.

This discovery represents a break-through of major significance to the practice ER and EW, although based upon principles which have been well known for some time: it is their significance in the present context which, apparently, has hitherto been overlooked.

In the electroplating industry -which aims at adhesive deposits -it has been long recognised that polished surface require special preparatory treatment to prevent poor adhesion or blistering of the electrodeposit. The plating -so it was thought would not adequately be "keyed" onto the "BEILBY -Layer" produced by intensive polishing, and named after G. T. BEILBY who, in 1904, originated the well-known "amorphous layer theory". This postulates that when a crystalline body, such as a metal, is cold-worked by polishing or burnishing, the surface layers of the exposed crystalline formation are caused to flow, and that the flowed metal layer is no longer composed of orderly arranged crystals but of randomly situated atoms. The actual truly amorphous "Beilby layer" is situated at the surface extremity and has a thickness of some 30-40Å, readily penetrable by the fine etchants whereby the plater hoped to achieve the key for proper adhesion -but in practice this remedy was unreliable. It was in 1947 that A. T. STEER first published the results of extensive research work carried out for THE ROVER COM-PANY, LTD., in a paper containing remarkable photomicrography of, and entitled "The Mechanism of Exfoliation of Electrodeposited Surfaces" and read at the Third International Conference of Electrodeposition held in London that year. Aided by metallography of a standard unsurpassed and rarely (if ever) equalled, (the technique was developed by P. BOTT of The Rover Company, Ltd.), STEER's findings led him to conclude that there were three main types of exfoliation, viz.: (a) stress exfoliation, (b) chemical or corrosion exfoliation, and (c) the combination of these, which he termed "stress-corrosion exfoliation". (Exfoliation due to operators' errors, such as inadequate cleaning, or electrolyte-contamination, etc. was not part of the investigation). Starting from the precept that \*Coldworking of a metal surface entails the absorption of energy by that surface", STEER showed that, even after most meticulous preparatory cleaning of the surface, it happened that "the electrodeposit just

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sheds itself completely, leaving a discoloured surface beneath. "He concluded that "this form of exfoliation may be termed "stress exfoliation", as it is due entirely to the relief of locked-up stresses..."

It clearly follows that, converseley, this selfsame absorbed energy would under controlled conditions -be instrumental in the production of nonadherent electrodeposits as are required in ER and EW.

When such a relatively thin (1.0-1.2mm) metal plate is subjected to such an intensive cold-working process as "rigidizing", then the structural change, i.e. grain-refinement, must-necessarily and by definition -extend throughout the entire thickness of the plate, so as to make it more rigid: here it is not merely a case of superficially absorbed energy, but of deep, penetrative absorption which remains unaffected by surface-preparation such as etching. From STEER's findings, one would expect "stress exfoliation" of any electrodeposit applied to such a plate -and this is precisely and advantageously what occurs in practice under normal conditions of ER and EW of (e.g.) copper onto a rigidized mother-blank of AISI St. 304.

Demonstrably, any intensive cold-working procedure will give similar results in terms of strippability enhancement, nor is the application limited to any particular grade of stainless steel or any metal. The degree of cold-working whereby the desired results may be achieved will obviously be in direct proportion to the thickness and nature of the metal concerned: in practical terms, therefore, it must be assumed that the cost-advantage of using thin sheet which-by whatever method of intensive cold-working is employed -will necessarily become rigidised thereby, will be a deciding factor.

It may also be expedient to rigidise the matrixplates by means of (e.g.) a press (used in lieu of, or in conjunction with, rolling as now employed for production of rigidized sheet for architectural purposes, etc.), to incorporate relatively flat edge-portions which would facilitate the attachment of edgeprotectors. Moreover, the provision of (at least) one flat edge-portion extending over the horizontal width of the plate (i.e., at right-angles to its direction of travel during "roller-rigidizing") is feasible when the rigidizing rollers can be raised clear when all but the final portion of the plate has been rigidized: this will facilitate the attachment (e.g., by seam-welding) of the matrix-plate's upper carrier/busbar.

Intensive cold-working to achieve rigidising may result in an "undulating" sectional outline of the plate. In one preferred arrangement, a rigidizing pattern of rhombic or oval "lozenge" shapes is embossed on staggered pitch to form concave "valleys" on one face of the plate, with corresponding convex "peaks" resulting on its opposite face.

The electrodeposit would not be readily detachable if it enveloped the plate, so that edgeprotectors need to be fitted, before use, to prevent envelopment.

It is well known metallurgically that the rigidity of a thin metal plate may be much increased by cold-working/work-hardening -indeed, the thin and usually very ductile electrodeposited copper starter-sheets may be stiffened, e.g., by embossing a pattern by means of a press, or by passing the sheet through embossing or corrugating rollers, so that these starter-sheets will be flat when placed between the anodes in the cell, to be plated to "commercial" thickness. For this purpose, however, edge protectors are not needed. It is a fact also that metals such as stainless steel, and especially titanium, in the as-rolled and bright-annealed condition, are inherently much less ductile than electrodeposited starter-sheets, and special facilities and techniques are required to produce a suitably work-hardened thin plate: these techniques have been developed by only a very few specialist establishments, such as RIGIDIZED METALS LTD.of Enfield, Middlesex, England, but rigidised sheetmetal is used chiefly for architectural and decorative applications. The maximum thickness lending itself for rigidising by the presently available methods seems to be limited to 16 swg or 1.6mm.

However, the aforementioned knowledge has in no way influenced electrodeposition techniques and operators have accepted the drawbacks of conventional blanks as unavoidable and that no obvious increased production and/or cost-savings can be made -e.g., operators have for years continued to use 3-4mm thick, as-rolled, stainless steel plates, when, by cold-working to achieve rigidizing in accordance with the invention, a 1.2mm thick stainless steel plate could be used at much reduced first-cost, and, surprisingly, with minimisation if not total elimination of surface-passivation treatment before each deposition-cycle.

It is yet a further advantage of a rigidizing pattern as herein described, that the metal layer electrodeposited thereon will not prematurely slide off vertically from a rigidized blank's surface, as may (and, indeed, at times does) happen with readily-strippable deposits upon a smooth, non-patterned blank. The "non-slip" surface resulting due to the rigidizing pattern prevents premature

vertical sliding-off even of electrodeposits approaching "commercial" thickness and of substantial weight -which is a very important advantage especially with "permanent cathodes" such as are used in (e.g.) the ISA PROCESS where upwards of 45kg of copper is deposited on each face of the blank.

By way of typical example (but by no means confined thereto) a suitable mother-blank's "blade" may be of 1.2mm thick sheet-metal with a rigidizing pattern of rhombic or oval "lozenge" shapes arranged on a staggered pitch embossed thereon, so that on one face of the sheet, concave "valleys" are formed, with corresponding convex "peaks" protruding on the opposite face, and resulting in an undulating sectional outline. Conventional, straightedged edge-protector channels would contact only the high spots, disadvantageously allowing electrolyte freely to penetrate into the gaps and valleys. In the aforementioned EDGEWISE system (GB Patent 2080829), adhesive tape serves as a gasket. Polyester tape coated with a thermosetting rubberbased adhesive normally is preferred, even though polyester has limited ductility: the latter suffices, however, to enable this tape to be applied to follow the said undulations and cover all but the deepest of valleys. Among several known rigidizing patterns produced by Rigidized Metals Ltd., and having suitable valley-depths, their pattern designated under reference "5WL" (oval "lozenge" shapes) and pattern reference "7GM" (rhombic shapes) have both been found satisfactory. After the tape has been applied to the blank's edge-portion, the latter should be heated to 80-90°C for some 5-10 minutes to ensure optimum adhesive strength from the tape's thermosetting adhesive coating: while heated, the polyester tape expands at a greater rate than the underlying metal, so that coverage of the valleys is aided, while the tape's tensile strength suffices to prevent tearing when contracting during cooling to ambient. It is advantageous to apply the tape under pressure to ensure penetration down into the valleys. In practice, it is expedient to apply at least two consecutive layers of tape.

Depending upon the width of the inner jaws of the EDGEWISE edge-protector's profile-strip, a thin strip of (e.g.) neoprene or nitrile packing may be applied to one or both faces of the tape-covered edge-portions of the blank, before the profile-strip is superimposed and subsequently fastened by snap-fitting its spreader-bar(s). The neoprene packing is especially advantageous with the "7GM" rigidizing pattern which due to the non-rounded

rhombic "diamonds" (rather than "lozenge" shapes) presents more abrupt outline-changes: these are "softened" by the compressed neoprene packing, i.e., the outline will be less "wavy".

Exceptionally, it may be necessary to employ a rigidizing pattern with deeper "valleys" than "5WL" or "7GM". The greater depth may be necessary when the blank's surface-area is greater than the conventional 1m \* 1m, and extra rigidizing may then be called for; the weight of the electrodeposit on permanent cathodes may also necessitate the use of deeper "valleys" to maintain proper "grip" on the heavy layers. In such cases, polyester tape has insufficient ductility to give complete coverage right down into these deeper valleys, and it is necessary to use a different method of gasketting the edge-portions of these matrix-plates.

RIGIDIZED METALS LTD. pattern reference "6WL" has deep oval valleys, and was used in a matrix-plate which had 55kg of copper electrodeposited on each face, i.e. a total of 110kg, at high current-density.

The deep valleys of this "6WL" and similar patterns may effectively be gasketted by applying a suitable plastic coating: techniques available for . the application include, e.g., "powder coating" and there are a number of suitable polymers which may be used, including polyester (which seems a logical choice), or polyvinyledene fluoride (PVDF). Brittle fillers should be avoided, and these include certain epoxy compounds. Adhesion of (e.g.) powder-coated polyester is aided by the very depth of the recesses in the pattern, so much so as to make it difficult to trim back any excess width of coating: the latter must not, of course, protrude beyond the inner jaws of the subsequently applied EDGEWISE profile-strip. Special care has to be taken during application of the polymer-powder so as to limit the coating-width, e.g. by means of masking-tape. It is best to apply two layers of polymer, so as to make the effective recess-depth sufficiently shallow thereby to be covered by at least one layer of the adhesive polyester tape which is applied over the plastic coating, in the manner already described.

There are other coating compounds than those hereinbefore referred to by way of example, which may be used to reduce the recess-depth so as to permit of subsequent tape-application. For example, certain hard rubber-compounds may be used: synthetic rather than natural rubber is preferred, as the latter may in time deteriorate and/or become electrically conductive. The adhesion of the said compounds (which are usually applied in thicker layers than, e.g., powder-coatings) may be strengthened by drilling holes through the "valleys" of

the pattern, before applying the compound, so that the latter extends from one face of the plate, through the holes, to combine with the coating on the opposite face. After curing, it may be necessary to dress such relatively thicker layers, to eliminate any lumps, and (ideally) to achieve flatness, before the tape is applied and heated, and the EDGEWISE profile-strip and spreader-bar are finally fitted, to provide permanent edge-protection to the matrix-plate.

The rigidized blank may be attached to its carrier/busbar by conventional methods. Stainless steel "permanent cathodes" as used (e.g.) in the ISA PROCESS are welded to stainless-steel carrier/busbars; careful alignment is essential, to ensure accurate positioning of the plate in use, where manipulation and stripping stages are fully automated. The plate's top-portion along its full width is advantageously left unrigidized i.e flat, so as to facilitate alignment and welding procedures. Attachment of the blade to its carrier/busbar thus presents no special mechanical engineering problems attributable to the rigidized plate as such -but there is another aspect to be considered, viz.:-

Electric current (D.C.) is carried from the underside of the busbar down to electrolyte-level, i.e. to the immersed portion of the "blade", typically over a vertical unimmersed distance of (e.g.) 100-110mm. In ER/EW, Faradav's Law may be paraphrased as "Volts cost money, Amperes are for free": a given amperage will deposit a certain amount of metal (= of saleable end-product), and any increase in voltage required to yield that amperage will increase the wattage, i.e. the energycost, accordingly. It follows, therefore, that the voltage-drop (dV) over the aforesaid vertical unimmersed distance of -e.g -100-110mm represents a significant cost-factor. All other things remaining equal, it follows from Ohm's Law that dV is inversely proportionate to the cross-sectional area -(c.s.a.) of a conductor of a given length. If, e.g., a 1.2mm thick rigidized "blade" is substituted for a 3mm thick flat, i.e. non-rigidized plate of the same material, then the c.s.a. of the non-immersed portion of the 1.2mm thick blade will only be 40% of that of the 3mm plate. The c.s.a. may be restored by means of one or more conducting-strips laminated in parallel to the non-immersed portion of the 1.2mm thick blade; in practice, however, it is not feasible to extend such laminations down to electrolyte-level: the increased thickness at or near that level would be likely to obstruct proper access of stripping-chisels and/or levers in automatic processing machines. Nevertheless, it is possible to compensate for any additional dV, by the method shown (for ease of presentation) in the following,

notional example. (NOTE: Ohm's Law suffices to give comparative values approximated to within adequate accuracy for the purpose of these illustrations). By way of example:

Existing stainless-steel matrix-plates used as permanent cathodes in Cu ER EW are 3.25mm thick, 990mm wide (overall), and have an effective immersed total (=2 faces) surface area of  $1.88m^2$ . The average current-density (CD) is  $250A/m^2$ : then, a total of 470A per plate is conducted over a vertical, non-immersed portion of the blade, i.e. from underside of busbar to liquid-level, a distance of 110mm; the voltage-drop in these conditions is acceptable. The resistivity of the stainless-steel - (AISI St.304) is  $70.0\mu\Omega$ -cm, the c.s.a. of the 11cm long conductor is  $(99 \times 0.325) = (say) 32cm^1$ , and the current is 470Amps: then, applying Ohm's Law:

the "acceptable" voltage-drop, in millivolts, may be calculated:  $dV = (0.001) \times (470/32) \times 11 \times 70 = 11.3 \text{mV}$ ; this equates to 5.3W per plate, or 212kW if the total number of matrix-plates in the example were 40,000.

Substituting 1.2mm thick matrix-plates of AISI St.304 of the same overall dimensions, rigidized except for the topmost 75mm portion of the blade, then: the effective total immersed surface-area of the two faces of the rigidized blade will be greater by ca.6.4%, and, assuming that the CD remains at 250A/m², a total current of 500A will be carried by the non-immersed portion of the blade: the topmost (non-rigidized) 7.5cm portion having a c.s.a. of (99 x 0.12) = 11.88cm², and the remaining rigidized portion of 3.5cm down to liquid-level having a c.s.a. of some 12.25cm². Applying Ohm's Law for each of these portions in turn, thus:-

 $dV' = (0.001) \times (500/11.88) \times 7.5 \times 70 = 22.10 \text{mV}$ ; and

 $dV'' = (0.001) \times (500/12.25) \times 3.5 \times 70 = 10.00 \text{mV}$ ; a sum-total of 32.1 mV, an excess of 20.8 mV over the acceptable level. (The extra power for 40,000 plates would amount to some 416 kW due to the additional dV).

If a 2.5mm thick metal-strip, 99cm wide and 7.5cm long, is laminated in parallel to the 1.2mm thick non-rigidized topmost portion of the blade, the total c.s.a. over the 7.5cm would be increased to 36.63cm²: as a result, dV' would be reduced to 7.16mV; in fact, with laminated conductors in parallel, there would be a further enhancement of some 10%, i.e.dV' = ca.6 4mV. Thus, in the foregoing example, the sum-total dV' + dV" would amount to 16.4mV -an excess of 5mV over the dV which has been assumed "acceptable", but which

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applied for a current of 470A per plate (not 500A). It will be seen, therefore, that the actual extra power needed due to substituting rigidized 1.2mm thick blanks for flat 3.35mm thick plates, in the foregoing example would amount to some 2.35W per matrix-plate, or 94kW for 40,000 cathodes. - (The excess could be halved if the topmost laminated length were increased from 75mm to 82.5mm, with a remaining distance of 27.5mm down to liquid-level). Moreover, the conductivity of such an arrangement may be greatly enhanced - and the extra voltage-drop be all but eliminated -by electroplating the laminated (topmost) portion with 1-1.3mm thick Cu.

The invention will now be described in greater detail, by way of example, with reference to the accompanying drawings, in which:-

Figure 1 is a front elevation of a matrix-plate in accordance with one aspect of the invention attached to its carrier/busbar in accordance with another aspect of the invention provided with edge protectors in accordance with a further aspect of the invention and immersed in a cell:

Figure 2 is an enlarged section on the line II -II of Figure 1;

Figure 3 corresponds to Figure 2 but shows the "blade" of the matrix-plate before its attachment to the carrier/busbar which is omitted for clarity:

Figure 4 is an enlarged section on the line III -III of Figure 1; and

Figure 5 corresponds to Figure 4 but shows a plate with a more deeply recessed rigidizing pattern coated with plastic and fitted with an edge protector, the latter being shown in outline only, for clarity.

In the drawings, a matrix-plate blade 1 is illustrated immersed in electrolyte the surface of which is indicated at 2, the blade 1 being generally rectangular and rigidized from its bottom-edge 3 up to an upper level indicated at 4 situate above the liquid-level 2, the blade's non-rigidized portion 5 continuing above the level 4 up to the underside 6 of the carrier/busbar 7. Two "windows" 8 may be cut out from portion 5 of the blade 1 for the purpose of access for lifting hooks and/or forklift prongs. The blade's non-rigidized portion 5 (except where/if cut out as aforesaid) is attached to one or more conductor-strips 12 by means of a plurality of rivets 13, leaving a gap 14 between the blade 5

and the conductor-strip 12, by means of spacerwashers 15 fitted to the rivets 13 as shown in Figures 2 and 3. After rivetting, the blade's nonrigidized portion 5 along its topmost edge is attached to the conductor-strip 12 by seam-welding as shewn in section in Figure 3, indicated at 16; the assembly is then attached to the underside 6 of the carrier/busbar 7 by seam-welding as indicated in section by 17, Figure 2. The assembly -being of stainless steel throughout -is copper plated to a thickness of 1.0-1.3mm, thereby to enhance conductivity of the non-immersed portion. The copper electrodeposit 18 extends down to a level 19 which lies approximately halfway between level 4 and electrolyte-level 2, all as indicated in Figure 3. The blade's 1 vertical side-edges 9 are provided with edge protectors 10 (as fully described in UK Patent 2080829) which may protrude above the liquidlevel 2 as shewn in Figure 1. To allow for ca.5mm differential thermal expansion, the protrusions 11 must terminate some 6mm below the level 19 of the copper plating 18. The blade's horizontal bottom-edge 3 is also provided with an edge protector 10 (as described in UK Patent 2080829) which must be free to expand laterally in both direction as depicted in Figure 1.

In Figure 4, multiple layers of self-adhesive polyester tape 20 are shewn applied to a side-edge 9 of the matrix-plate's blade 1, and a neoprene packing-strip 21 is fitted on top of the tape-layers 20 on one face of the blade, before the profile-strip 22 and the spreader-bar 23 of the edge protector 10 are applied as described in detail in UK Patent 2080829.

In Figure 5, a blade 1 is depicted having a rigidizing pattern with relatively deeper recesses 24. This greater depth is compensated for by means of a suitable plastic coating, such as (e.g.) by powder-coating with a suitable polymer such as, e.g., PVDF or polyester, or by applying a corrosion-proof synthetic rubber coating; the coating 25 reduces the depth of the recesses 24, and its adhesion to the underlying metal may be greatly enhanced by drilling holes 26 at suitable intervals along the edge-portion of the blade1 before applying the coating material: the latter will penetrate through the drilled holes 26, and, during thermal treatment and curing, the plastic coating 25 on both faces of the blade 1 will be fused integrally with the interconnection through the drilled holes 26, so that the coating 25 on one face of the blade 1 is held by that on the opposite face and neither can be peeled off. Tape 20 may then be applied on top of the plastic "fillings" 25, and the edge protector 10 may be fitted, in the usual way as described in detail in UK Patent 2080829.

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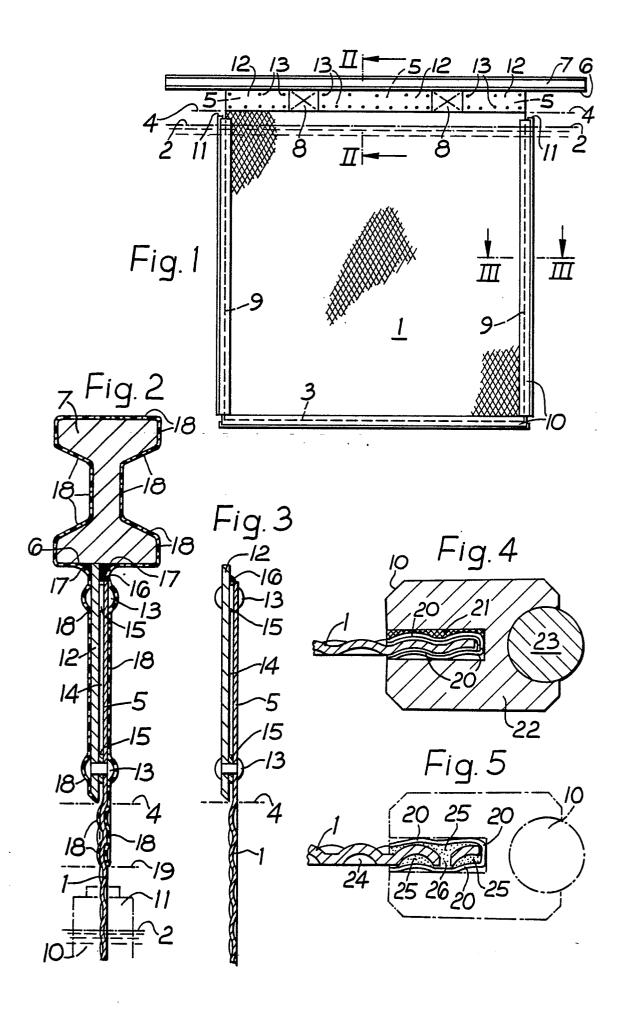
#### Claims

- 1. A mother-blank matrix-plate (1) to receive upon its surface electrolytically-deposited layers of metal and/or of a metal-rich compound such as a metal-oxide, which layers are readily detachable from that surface, by virtue of the said mother-blank matrix-plate during its manufacture having undergone a process of cold-working of such intensity as to significantly reduce the grain or crystal size right through the thickness of the said mother-blank matrix-plate (1) thereby evidencing the absorption of free energy in its crystal-structure.
- 2. A mother-blank matrix-plate as claimed in Claim 1, characterised in that the intensive cold-working as therein described is achieved by a process known as "rigidizing" whereby a certain pattern is embossed, rolled or stamped upon the mother-blank matrix-plate (1).
- A mother-blank matrix-plate as claimed in Claim
   or Claim 2, characterised in that the matrix-plate is made of rigidized sheet-metal.
- 4. A mother-blank matrix-plate as claimed in Claim 3, oharacterised in that the sheet-metal is titanium.
- 5. A mother-blank matrix-plate as claimed in Claim 3, characterised in that the sheet-metal is a stainless-steel, including but not confined to such specifications as, e.g., AISI St.304, AISI St.304-L, AISI St.316, AISI St.316-L, or AISI St.318 (or their equivalents).
- 6. A mother-blank matrix-plate as claimed in Claim 5, characterised in that the matrix-plate (1) is made from rigidized bright-annealed or annealed + pickled stainless steel.
- 7. A mother-blank matrix-plate as claimed in Claim 3, characterised in that the sheet-metal is aluminium or an aluminium alloy.
- 8. A mother-blank matrix-plate as claimed in any preceding Claim, characterised in that the matrix-plate (1) is fitted with edge protectors (10) these incorporating an insulating material which is thermally bonded to the metal surface of the mother-blank matrix-plate (1).
- 9. A mother-blank matrix-plate as claimed in Claim 8, characterised in that the thermally bonded insulating material is polyester tape (20) pre-coated with a rubber-based thermosetting adhesive.

- 10. A mother-blank matrix-plate as claimed in Claim 8 or Claim 9, characterised in that the insulating material is based on polyester or on polyvinyledene-fluoride ("PVDF") as a polymer suitable to be applied to the metal by the process known as "powder coating" prior to thermal treatment.
- 11. A mother-blank matrix-plate as claimed in Claim 10, characterised in that its edge-portions (3, 9) prior to being powder-coated are selectively drilled through thereby to enable the polymer-powder (25) to penetrate through the drilled holes (26), so that, after thermal treatment, the plastic layers on both faces of the mother-blank matrix-plate (1) will be integrally interconnected through these drilled holes (26) thereby providing mechanical bonding between these layers and enhancing their adhesion.
- 12. A mother-blank matrix-plate as claimed in any preceding Claim, characterised in that the topmost portion (5) of its "blade" along its full width and which, during electrolytic deposition, is adjacent a carrier/busbar (7), is flat and has no pattern embossed thereon down to a level of at least 25mm above electrolyte level (2), and has at least one conductor-plate (12) of similar horizontal and vertical dimensions connected parallel to it to form a non-immersed laminated conductor which is attached to the busbar (7) and which, due to its greater cross-sectional area and current-carrying capacity, in use, substantially reduces any voltagedrop between the busbar (7) and the blade's immersed portion.
- 13. A mother-blank matrix-plate as claimed in any preceding Claim, and used as an anode or cathode or bipolar electrode in the electrodeposition of metal or of a compound rich in metal such as an oxide.
- 14. A mother-blank matrix-plate as claimed in Claim 13, and used cathodically for the production of so-called "starter-sheets" in electrorefining and/or electrowinning processes.
- 15. A mother-blank matrix-plate as claimed in Claim 13, and used as a so-called "permanent cathode" for electrodeposits of so-termed "commercial thickness" in metal electrorefining and/or electrowinning processes.
- 16. Any process for the electrodeposition of readily detachable layers of metal or of a compound rich in metal such as an oxide, and employing a

mother-blank matrix-plate (1) as defined in any preceding Claim.

17. The product of any process as claimed in Claim 16.





# **EUROPEAN SEARCH REPORT**

EP 86 30 2613

Category		th indication, where appropriate, vant passages	Relevant to claim	CLASSIFICATION OF TH APPLICATION (Int. CI.4
X	GB-A- 552 978 MANGANESE CORP.) * Page 1, lines lines 99-124; cl	30-44; page 2,	15-17	C 25 C 7/0
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	* Abstract *		,	
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## **EUROPEAN SEARCH REPORT**

EP 86 30 2613

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