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MASKED ELECTRODE STRUCTURE AND PROCESS FOR ELECTROLYTIC DEPOSITION OF METALS

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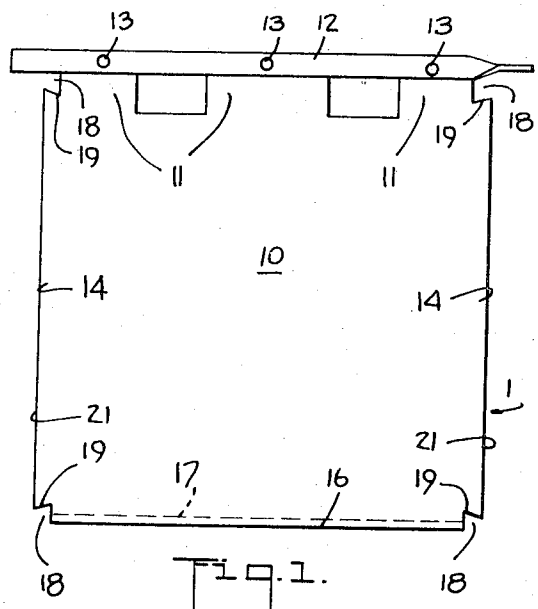



Fig. 1.

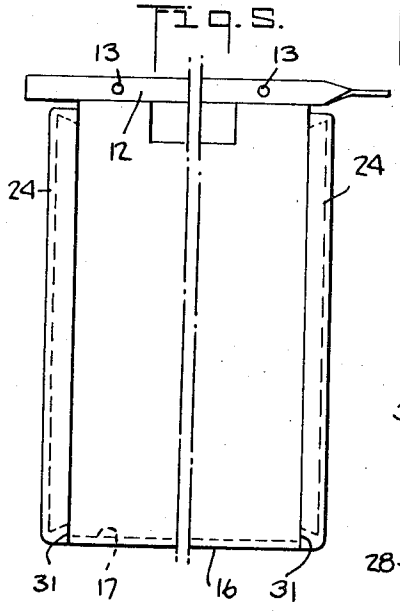



Fig. 3.

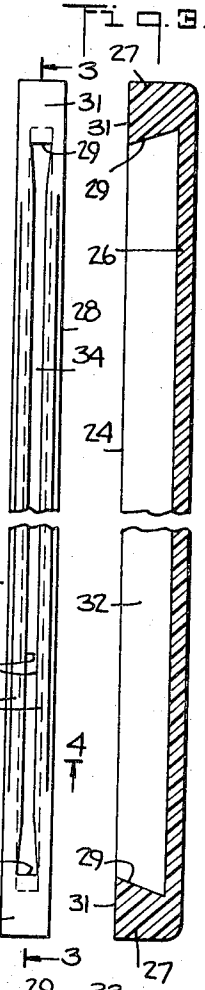
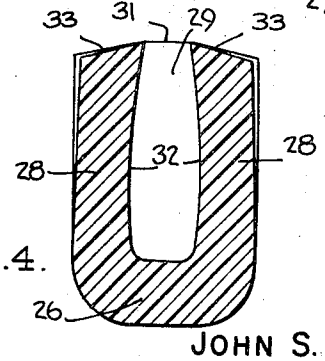



Fig. 2.




Fig. 4.





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# MASKED ELECTRODE STRUCTURE AND PROCESS FOR ELECTROLYTIC DEPOSITION OF METALS

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Continuation-in-part of abandoned application Ser. No. 104,981, Jan. 8, 1971. This application July 12, 1972, Ser. No. 271,154

Int. Cl. C22d 1/16

U.S. Cl. 204—12 8 Claims

## ABSTRACT OF THE DISCLOSURE

The invention is directed to the electrolytic deposition of metals and particularly to a novel masked cathode structure upon which metal is deposited. The mask comprises a removable, shrink-fitted, corrosion resistant, insulating member which envelops the vertical side edges of the cathode and substantially seals said vertical edges from contact with the electrolyte. Retaining surfaces on the vertical cathode edges mate and lock on to complementary surfaces within the masks. The bottom edge of the cathode is provided with a V-shaped groove whereby a plane of weakness is formed in the electrodeposit at that point.

The present application is a continuation-in-part of U.S. application Ser. No. 104,981, filed Jan. 8, 1971, and now abandoned.

While the present invention is applicable in the electrolytic deposition of various metals, the impetus for the invention arose in the field of copper refining and, consequently, the description which follows draws primarily upon the experience had in that field. In the electrolytic refining of copper as it is presently practiced, the copper is deposited upon thin sheets of high purity copper known as starting cathodes or starting sheets. These starting sheets are produced by electrolytically depositing copper for a period of about 24 hours on rigid mother blanks of rolled copper. The deposits form on both faces of the blanks and the thin copper sheets thus deposited must then be stripped from the blanks. After stripping, these starting sheets are placed in an electrolytic refining cell with crude copper anodes where relatively heavy deposits of copper are formed on the starting sheets. When the copper deposition step has been completed, the starting sheets with the copper deposited thereupon are melted into ingot or bar or other suitable forms of high purity copper for further processing.

More recently, it has been proposed to deposit copper directly from the anode upon a suitable cathode blank for prolonged periods to obtain heavy deposits of high purity copper and thereby obviate the necessity for producing and employing intermediate starting sheets. Such heavy deposits must also be stripped from the cathode blanks.

The stripping operation is made more difficult and costly if copper deposited on the cathode edges joins the two face deposits. Where starting sheets are produced, various means are used to strip the face deposits from the cathode blanks generally leaving the edge deposits behind. These edge deposits then require a separate stripping operation, and the edge copper thus stripped is largely scrap which may be remelted as anode copper and again undergo electrolytic refining. In the case where heavy deposits are formed, the thick plate which envelops the blank effectively prevents stripping. A practical and economical edge masking for cathode blanks which would prevent the deposit of copper at the cathode edges has long been sought. A number of cathode structures and materials have been used in efforts to achieve masking of the cathode edges with results which have not been entirely successful.



We have now made a novel cathode structure including special insulating masking members of unique configuration which overcomes the disadvantages of the known prior art cathode structures and greatly facilitates the stripping operation in the electrolytic refining of metals.

It is an object of the invention to provide for the electrolytic refining process a cathode structure which includes insulating masking members.

It is another object of the invention to provide insulating masking members for the edge portion of cathodes having a novel configuration.

It is still another object of the invention to facilitate the stripping of copper deposits from the cathodes in the electrolytic refining of copper.

Other objects and advantages of the invention will become apparent from the following description taken in conjunction with the accompanying drawings in which:

FIG. 1 shows a side elevational view of a cathode structure made in accordance with this invention.

FIG. 2 is a plan view of the insulating masking member of this invention.

FIG. 3 is a cross-sectional view of the insulating masking member taken along the line 3—3 of FIG. 2.

FIG. 4 is a cross-sectional view (enlarged) of the insulating masking member taken along the line 4—4 of FIG. 2.

FIG. 5 is a side elevational view (broken) of a cathode structure with insulating masking members mounted thereon.

Generally speaking, the invention is directed to a novel cathode structure having specially shaped vertical side edges and a pair of insulating masking members mating with the vertical side edges of the cathode in shrink-fitted relation thereto. In this connection, the term "shrink-fitted" as used herein, means the fit obtained primarily by elastic shrinkage, by first stretching the masking members at ambient or elevated temperature, installing the members in the stretched condition on the cathode blank and then releasing the members into engagement with the cathode blank whereby the members remain under residual tension as installed. Heating the masking members may facilitate the stretching and fitting operation, but it is not essential that the masking members be heated.

Referring now to FIG. 1 of the drawing, it will be seen that in the cathode structure **1** cathode blank **10** is provided with lugs **11** at the top thereof. The cathode blank **10** may be formed of rolled copper, or any other metal or composite structure capable of resisting the corrosive environment of the plating bath and transmitting the plating current. It is advantageous however to form the cathode blank of an acid resistant material such as titanium or ferritic or martensitic stainless steel having a linear coefficient of expansion significantly lower than that of copper. The cathode blank customarily has a thickness of from 1/16 inch to 3/8 inch. Lugs **11** are attached to the conductor bar **12** by appropriate fastening means such as, for example, rivets **13**, or by bolting or welding. The bottom edge **16** of the cathode **10** is provided with the customary inverted V-shaped groove **17**. The vertical side edge portions **14** of the cathode **10** have a dove-tailed configuration as seen in FIG. 1. This configuration was achieved by the provision of the notches **18** at the ex-

tremities of the vertical edge portions **14**. These notches **18** are defined at one side thereof by inclined surfaces **19** which form an angle of less than 90° with the edge surface **21** of the edge portion **14**.

It is upon these dove-tailed portions **14** that the insulating masking members **24** of FIGS. 2 through 4 are positioned as shown in FIG. 5. As seen in FIGS. 2 through 4, the insulating masking members **24** have a channel **34** therein formed by a bottom wall **26**, a pair of side walls **28** and a pair of end walls **27**. The inner surfaces **32** of the side walls **28** are concave so that, as seen in FIG. 4, the mouth opening of the channel is slightly smaller in width than the bottom wall **26** of the channel. These side walls **28**, having a thickness of at least 0.02 inch, and, more usually, from 1/16 inch to 1/4 inch, are resilient so that they can be flexed to widen the mouth opening as required. The inner surfaces **29** of the end walls **27** are inclined so that the bottom of the channel has a somewhat greater length than the top of the channel, and the angle between the inner surface **29** of the end wall **27** and the end wall top surface **31**, is less than 90°, e.g., 75°. Thus, the longitudinal cross-section of the channel provided by the insulating masking member as seen in FIG. 3 is dove-tailed in shape, and thereby adapted to mate with the similarly shaped edge portions **14** of the cathode **10**. It will also be noted, as seen in FIG. 4, that the side wall top surfaces **33** of the side walls **28** are so inclined that the angle between the said side wall top surfaces **33** and the inner surfaces **32** of the side walls **28** is substantially less than 90°. The overall dimensions of channel **32**, both as to length and width, i.e., between opposed top surfaces **31** and **33**, are slightly smaller than the dove-tailed shaped edge portion with which they must mate. The insulating masking member, advantageously formed of polypropylene, is stretched over the extremities and lateral faces of the dove-tailed shaped edge portion **14** of the cathode **10**.

The materials used for insulating strip or masking members should have a low modulus of elasticity to permit the requisite stretching and should be hydrophobic to prevent electrolyte from reaching the masked surface of the cathode blank. Thus, the insulating masking members may be formed of other non-conductive corrosion resistant materials such as fluorocarbons, polyethylenes, polycarbonates, ABS resins, polyvinyl chloride and copolymers thereof.

When the stretched insulating masking member has been positioned on the cathode blank and released, a snug shrink fit is obtained and the complementary mating inclined surfaces **19** and **29** of the cathode and insulating masking member, respectively, are in locking engagement, preventing accidental dislodgment of members **24** during inspection and stripping or during thermal cycling which results from alternating plating and stripping. It will also be noted that the sharp edges provided along the channel opening of the insulating masking member **24** provide a line contact with the cathode faces along the lips of the channel which effectively prevents copper from building up under member **24**. One top surface **31** of each masking member butts firmly against one end of bottom edge **16** to seal the end of the V-shaped groove **17**.

The thus formed cathode blank is employed in a copper electrofined electrolyte comprising essentially an aqueous solution of copper sulfate and sulfuric acid maintained at a temperature of at least about 130° F. and advantageously about 150° F. Cathode current density is usually of the order of about 20 amperes per square foot. In operation, the pair of insulating masking members enveloping the side edges of the cathode effectively prevent deposition of copper along the edges of the cathode. Further, the V-shaped groove at the bottom edge of the cathode causes the copper to deposit at this edge in the form of dendrites which grow in directions normal to the sides of the V-groove. Where the dendrites meet in the course of their growth a plane of weakness is established. In stripping the deposited copper from the two faces of the cathode, the copper separates from the faces following the sharp edges of the masking members, and as the stripping operation proceeds toward the bottom edge of the cathode, the copper deposited at the bottom edge will fail along the aforementioned plane of weakness and the face deposits are separated from the cathode. After the copper has been stripped from the cathode blanks, the cathode blanks are returned for use in the refining process.

In electrolytic refining, it is a common practice to coat the faces of the cathode blank with a parting film such as oil or other suitable compound to facilitate the stripping operation, and such coatings may be used on the cathodes of the present invention if such is required to ensure parting of the deposited metal from the substrate. However, it has been found that it is unnecessary to provide titanium cathode blanks with such a coating. The naturally occurring oxide film on titanium plus the difference in expansion characteristics of copper and titanium tend to provide ease of separation of the deposited metal from the substrate even without use of a parting film. In some cases it is additionally desirable to protect the edge portions of the cathode which will lie beneath the insulating strip members with an adherent tape, such as polyethylene, fluorocarbon, polyvinyl chloride, and copolymers thereof or polyester film, or by coating the edges with an insulating medium such as silicone grease or a fluorocarbon suspension to further assure that deposition of copper will not occur under the insulating strip member. Such insulating means applied directly to the edge portions of the blank accommodates irregularities or variations in surface condition and acts as a gasket between the contact edges of the strip member and the blank.

By way of example, cathode blanks formed of stainless steel and being, overall, 41 inches in vertical length, 38½ inches wide and ⅛ inch thick with dove-tailed shaped vertical edge portions, were shrink fitted with insulating masking members formed of polypropylene.

The length of the vertical side edges of the dove-tailed portions of the cathode blank was 40 inches. Measured from the vertical side edges, the notches at the upper end of the dove-tailed portion were ½ inch deep, while the notches at the lower end of the dove-tailed portion were 29/64 inch deep. The notches at the lower end of the dove-tailed shaped portions of the cathode blank were initiated at a point on the vertical side edges just 9/64 inch above the bottom edge of the cathode blank. The angle between the edge surface of the vertical side edges and the inclined surface which defines one side of the notch was 75°. The length of the bottom edge was 37 19/32 inches and the inverted V-groove therein was 0.040 inch to 0.050 inch deep at the apex thereof with an angle of 90° between the walls of the groove.

The overall dimensions of the insulating masking member were 40 inches long and 0.380 inch wide. The bottom walls were ⅛ inch thick. The side walls were ⅛ inch thick adjacent the bottom of the channel and somewhat less than ⅛ inch thick above that level. The end walls were ½ inch thick at the channel opening tapering to ⅜ inch thick at the bottom of the channel. The depth of the channel was 7/16 inch, while the length of the channel opening was 39 inches and the length of the channel at the bottom thereof was 39¼ inches. The width of the channel opening was ⅛ inch adjacent the ends thereof, but within ½ inch of the said ends the channel opening narrowed to 3/32 inch, which width prevailed over the rest of the length of the channel opening.

In fitting the insulating masking members on the cathode blanks the masking members were immersed in water at a temperature of about 190° F. for about 5 minutes. In this condition the masking members were readily stretched (up to 1¼ inches in length) over the dove-tailed side portions of the cathode and permitted to cool. After cooling, the masking members were found to be stretched

about ¾ inch and very securely mounted on the cathode with the contacting edges of the masking members and the cathode in sealing engagement.

Cathodes having insulating masking members fitted thereon and coated with a dielectric oil mixture were placed in a plating tank between crude copper anodes. The masking members extended from a point adjacent the bottom edge of the cathode to a point on the cathode above the level of the electrolyte. The electrolyte was composed of 40 grams per liter of copper and 200 grams per liter of sulfuric acid. The operating temperature of the bath was 150° F. A current density of 18.3 amperes per square foot was employed and the current was passed for a period of 13.3 days. At the end of the period, the cathodes were removed from the electrolyte and the copper deposited thereon was readily stripped without dislodging the masking strips. The stripped copper was smooth-edged at the surface which had been adjacent the masking members and had a thickness of about ¼ to ⅜ inch. The copper deposited averaged 295 pounds on each of the cathodes. The copper was of standard high purity suitable for melting and casting into ingot, wire bar or other suitable shapes. The insulating masking members were removed from a cathode for the purpose of examining the edge portion of the cathode. It was found that substantially no copper had been deposited in the area protected by the insulating masking members. This indicated that a sealing contact had been attained between the insulating masking members and the cathode.

There has thus been disclosed an electrode structure which enables substantial labor savings in starting sheet preparation and reduction of waste material in the electrolytic refining of copper.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. In a process for electrorefining copper wherein copper is electrodeposited on a cathode from a bath operated at about 150 °F., the improvement comprising employing as the cathode a structure including a thin, substantially rectangular cathode blank of a material selected from the group of titanium and ferritic and martensitic stainless steels having a removable, shrink-fitted corrosion-resistant insulating masking member enveloping the vertical side edges thereof and substantially sealing said vertical side edges from contact with electrolyte, a pair of retaining surfaces at the extremities of each of said vertical side edges, said retaining surfaces mating with complementary surfaces within said insulating masking members to thereby lock the insulating masking members on the cathode blank, whereby deposition of metal on the vertical side edges is prevented, the cathode blank being provided with a V-shaped groove in the bottom edge thereof.

2. A process as in claim 1 wherein the cathode blank is made of titanium.

3. A cathode structure specifically adapted for the electrolytic deposition of metals thereupon at temperatures of about 150° F., including a thin, substantially rectangular cathode blank having a removable, shrink-fitted corrosion-resistant insulating masking member enveloping the vertical side edges thereof and substantially sealing said vertical side edges from contact with electrolyte, a pair of retaining surfaces at the extremities of each of said vertical side edges, said retaining surfaces mating with complementary surfaces within said insulating masking members to thereby lock the insulating masking members on the cathode blank, whereby deposition of metals on the vertical side edges is prevented, the cathode blank being provided with a V-shaped groove in the bottom edge thereof.

4. The cathode structure of claim 3 wherein the insulating masking members are formed of polypropylene.

5. A cathode structure as in claim 3 wherein the cathode blank is made of a material selected from the group of titanium and ferritic and martensitic stainless steels.

6. The cathode structure of claim 5 wherein the insulating masking members have bottom, side and end walls, the inner surfaces of which define an open, closed-ended channel which opens at the top of each member, the opening of the channel being defined by the top surfaces of the side and end walls, the inner surfaces of the side walls of the member being curved inwardly so that the width of the channel at the opening thereof is smaller than the width at the bottom of the channel, the side walls being sufficiently resilient so that they can be flexed to increase the length and width of the channel opening, the top surfaces of said side walls being inclined so that the angle between the top surfaces and the respective inner face of each side wall is less than 90° to provide a relatively sharp edge at the sides of the channel opening, the inner faces of the end walls being inclined inwardly of the channel from the bottom thereof to provide a sharp edge at the ends of the channel opening wherein the angle between the top surface and the inner face of each end wall is less than 90°, whereby a line contact is established between the insulating masking member and the cathode blank about the channel opening.

7. The cathode structure of claim 6 wherein the end walls of the insulated masking member comprise a pair of retaining surfaces which mate with a complementary pair of surfaces provided at the extremities of the vertical side edges of the cathode blank to thereby lock the insulating masking members on the cathode blank.

8. The cathode structure of claim 7 wherein the insulating masking members are formed of polypropylene.

**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,536,877 | 1/1951 | Emanuel et al. | 204—281 |
| 1,994,144 | 3/1935 | Merrill | 204—281 |
| 1,468,838 | 9/1923 | Schuh | 204—281 |

OTHER REFERENCES

Metal Industry, Dec. 18, 1953, vol. 83, p. 496.

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R. L. ANDREWS, Assistant Examiner

U.S. Cl. X.R.

204—108, 281