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PROCESS OF ELECTRODEPOSITION

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Fig. 1.

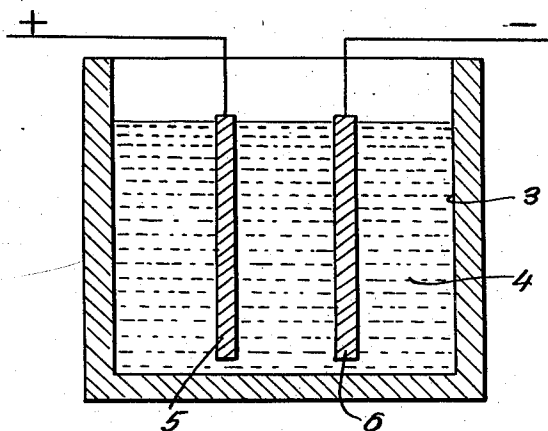
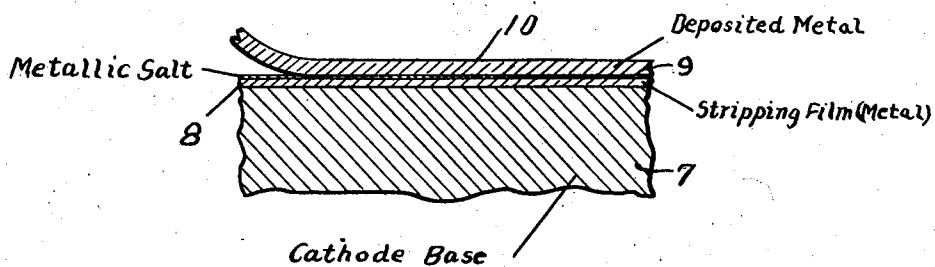


Fig. 2.



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PROCESS OF ELECTRODEPOSITION.

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This invention relates to a process of electrodeposition, and more particularly to a process for the production of metal articles in the form of sheets and the like, which are formed by electrodeposition on a cathode, the deposited material being removed therefrom by stripping when the deposit has built up to the desired weight and thickness. The invention further relates to an improved type of cathode so formed as to facilitate the stripping of the deposit therefrom.

In the electro-forming of articles of copper and other similar metals in which the deposited layer is removed from the cathode, which may be in the form of a starting sheet or of a revolving drum, it is difficult to remove the deposited layer from the cathode upon the completion of the deposition without injury. This is particularly true where the deposit is in the form of a thin plate and if the article formed by this deposition is to have an irregular contour or surface produced by making use of a cathode of appropriate form, the difficulty of stripping is greatly increased and in some instances it is almost impossible to remove the deposit without tearing or otherwise injuring it. Many attempts have been made, heretofore, to overcome these difficulties and many schemes for treating the cathode to permit the ready stripping of the deposit have been suggested.

According to some of these methods the cathode is treated with a dilute solution of a salt of selenium, and it has also been proposed to make use of a dilute tincture of iodine, and also weak solutions of silver nitrate. Other suggestions include applying a thin layer of graphite and also making use of oils such as ordinary engine oil. These various materials are applied to the surface of the cathode prior to its insertion in the electrolytic cell and the purpose of each of these schemes is to interpose between the deposit and the cathode a thin film of material which prevents too close an adhesion of the deposit to the cathode. These several suggested methods, however, are open to numerous objections, the principal objection being that they do not wholly serve the desired purpose of permitting easy stripping. In addition, many of the suggested materials are expensive and, furthermore, it is difficult to apply these materials so as to

form a thin uniform coating over the surface of the cathode. The use of such materials as those above mentioned frequently prevents or makes extremely difficult the deposition of a deposit of a uniform character and the sheet of deposited material is frequently full of pin holes and other small imperfections which are a great detriment when the deposit is unusually thin. The occurrence of pin holes is not only objectionable, but when a thin deposited layer is being made and pin holes occur in it, when the stripping operation is carried on, the sheet to be stripped is further injured because of tearing around the pin holes. Most of these materials also are not good conductors and because of this characteristic their use involves increasing the resistance of the cell and thereby adding to the expense of the deposition because of the larger amounts of power expended. For these various reasons it has been difficult, heretofore, to produce thin sheets of metal electrolytically by deposition on a cathode from which the sheets are later to be stripped and, so far as I am aware, there is no proposed method for this purpose which is, in all respects satisfactory.

I have found that these several difficulties in stripping may be overcome by applying to the cathode a thin surface film of metal other than that which is later to be deposited for the formation of the articles. For the best results this film should be quite thin and preferably of a metal which has less mechanical strength than the metal which is to be deposited thereon. If the metal is also one which has a relatively low melting point in comparison to the metal of which the article is to be made, the stripping process is greatly facilitated, as will presently be described. Also, it is desirable to make use of a metal for this film which is substantially inert to the electrolyte in which the cathode is to be introduced, or, if not wholly inert, the metal in the film should react with the electrolyte to produce a thin, uniform and adherent film of the metallic salt. It is highly desirable that the metal in the film should be in such a form that it has a crystalline structure and for this reason the application of the film by electrodeposition is probably the simplest and most inexpensive procedure. By such a process a small amount of the metal may be applied in a

thin, uniform and continuous layer and but little expense is involved on account of the small amount of material which is used and the small expenditure of power involved in depositing this material. In the case of electrodeposition of copper from a copper sulphate electrolyte, as, for instance, in the formation of sheets or other similar articles, I have found that the metal which is best used for the surface film is lead applied to the surface of the copper by electrolysis.

In order that the invention may be better understood, I shall now make reference to the accompanying drawings, in which—
Fig. 1 is a vertical cross-sectional view of an electric cell in which the present invention may be practiced, this cell being shown conventionally, and

Fig. 2 is an enlarged view in section of a portion of the cathode with the deposit partially stripped therefrom.

In these drawings the cell 3 may be of any convenient form and is here shown as provided with walls which are substantially inert to the electrolyte 4. The cell contains the usual anode 5, connected to the positive terminal of a source of power and a cathode 6 connected to the negative terminal.

The cathode 6 is illustrated on an enlarged scale in Fig. 2, and consists of a body or base 7 of any convenient material having suitable electrical and mechanical properties. This cathode may have a smooth surface if the deposit is to be made in the form of a sheet, or may be given an irregular surface when an article is to be produced having an irregular contour, such as might be formed by embossing. This cathode is to receive a film 8 of metal which facilitates stripping, and one convenient metal for the purpose is lead. The surface film of lead may be applied by electrodeposition in a cell in which the electrolyte contains lead in solution. The lead solution is preferably one to which the material of which the cathode body or base is inert, or at least soluble only with difficulty. If the cathode is made of copper, for example, a solution containing lead silica fluoride is satisfactory, and preferably the solution is one in which the lead content is about 9%, with 2% of hydrofluosilicic acid present. Solutions containing lead salts, such as leadfluoroborate and lead acetate can also be used, and may be desirable also for use in connection with the application of a lead film on an iron cathode. The choice of the lead solution will depend to a large extent on the character of the material of which the cathode is made, and the selection will be made with the object in view that the metal of the cathode shall not be detrimentally affected by this solution.

With a copper cathode blank to be coated in a solution containing lead and hydro-

fluosilicic acid, as above stated, the deposition of the surface film can be carried on with a small current density of from ten to fifteen amperes per square foot, with a resistance drop of one half a volt. The form of the cell and the other conditions will, to a large extent, depend on the size and shape of the blank to be coated and the deposition will be carried on until a thin film is produced. A film of lead of a thickness of .00025 inch is sufficient for ordinary stripping purposes although a film having a thickness as low as .0001 inch is capable of use. I do not wish to be confined to this lower limit of thickness, however, since I have found that stripping is easily done when the cathode receives a film which is almost infinitesimally thin. As to the upper limit, this will be largely dictated by reasons of economy, but ordinarily will not exceed .001 inches in thickness. When a film of the desired thickness has been applied to the cathode blank the latter is removed from the cell and any adhering electrolyte is washed from the surface. The blank is now ready for use in the main electrolytic process and is placed in the electrolytic cell in the usual way. For the deposition of copper on the cathode over the surface film, it is preferable to make use of an electrolyte containing copper sulphate, and the deposit of copper is built up to the desired thickness, then the cathode with its deposit is removed from the cell, and the deposit may be easily stripped from the cathode. Upon the introduction of the cathode with its lead film into the copper sulphate solution there is formed a thin film of lead sulphate which coats the stripping film. Over this film of the salt is deposited the layer of copper and the film of salt is very thin, while the film of deposited metal may be of any desired thickness.

In the stripping operation a number of methods may be used. For instance, it is possible to strip the deposit from the surface film simply by mechanical means, and it is found that the deposit will part easily from the cathode although parts of the thin film of lead may stick to the surface of the deposit as the latter is removed. Ordinarily this residual lead is not objectionable but if necessary the stripped deposit may be cleaned to remove it. Usually, however, the amount of lead which sticks to the surface of the deposit is so small that its presence is a matter of indifference. Under certain conditions mechanical stripping may be objectionable and it may be necessary to resort to heat treatment to facilitate the removal of the deposit.

For this purpose the cathode with its surface film and the copper deposit thereover, is heated and the application of the heat,

which may be either by hot air, by flame, or by steam, is confined as largely as possible to the surface of the main deposit. This application of heat causes this main deposit to swell and expand and the deposit appears to warp away from the cathode by reason of the expansion. The lead is not materially affected by the application of heat, although in this warping the swelling of the copper layer may cause some of the lead to be removed from the cathode with it. If desired, heat may be applied to the surface of the cathode to a sufficient extent to melt the lead film and the amount of heat required for this purpose is not sufficient ordinarily to affect the copper deposit injuriously. When the lead melts out from between the cathode and the deposit, the latter is wholly freed from the cathode. The application of heat sufficient to cause the melting out of the lead layer may be carried on either by the application of a flame or by passing a heavy electric current through the cathode. The heating effect of this current will cause a rapid melting of the lead and ordinarily without causing oxidation or discoloration of the copper. After the copper deposit has been removed from the cathode the latter is returned again to the lead bath and another thin film of lead applied to the surface thereof, whereupon the cathode is again placed in the main electrolytic cell and further deposition of copper produced.

While I have found that lead is the most useful metal for application to the cathode blank to facilitate the stripping of the deposit, by reason of its easy application and its low cost, which is an important factor in commercial practice, other metals may also be used in place of lead. These metals should preferably have a lower melting point than the metal of which the deposit on the cathode is to be formed, so that the stripping by means of the heat treatment may be resorted to, if necessary. Also the metals which are used for the film should be of comparatively low mechanical strength, since this also facilitates the stripping. Inasmuch as a very thin film of the metal is used on the cathode blank, it is desirable that the metal employed should be substantially inert to the electrolyte in the cell from which the main deposit is to be made, since otherwise the film might go into solution before the deposition could take place upon it. With this characteristic of inertness in mind, the metal will be selected with reference to the electrolyte which is to be used in the final deposition process and various metals will occur to the metallurgist as being suitable for the purpose. For instance, in the electrodeposition of copper from a copper sulphate solution, silver could well be used, in so far as the desired stripping result is concerned, although the cost would or-

dinarily be prohibitive. Zinc, if sufficiently pure, could also be used for the purpose, although it is difficult to secure perfectly pure zinc and if impurities occur in it local electrolytic action sets in which causes the film to be pitted, thus rendering it difficult to make a perfect deposit over the film.

As copper is the metal which is handled electrolytically probably to the greatest extent, undoubtedly lead will be most used for the production of the film, and I have found that lead is most satisfactory for the purpose when applied by electrolytic methods. For instance, I have made use of a lead sheet for the cathode which was polished so as apparently to be without surface imperfections and have then employed this lead sheet as a cathode in an electrolytic cell, but this polished sheet of lead is by no means so satisfactory as a cathode of any suitable type covered with a thin film of lead electrolytically deposited. This leads me to the belief that it is the crystalline structure of the electrolytically deposited metal which affords the vast advantages of this type of film over those applied in other ways. I have found that lead applied by methods other than electrolysis is useful when the stripping is to be carried on by the application of heat, but for mechanical stripping, which is, of course, much simpler and easier, the electrolytic lead is vastly superior to any other form of the metal.

A further important advantage in the use of the lead for this cathode film, especially in connection with the electrodeposition of copper, resides in the fact that the lead is substantially inert to the electrolyte which contains the copper sulphate usually employed in such electrolytic work. Lead is not readily soluble in the free-sulphuric acid which is present in the electrolyte, although it is probable that a thin film of lead sulphate is formed. This thin film of the lead salt is not detrimental, however, because it appears to be continuous and uniform and closely adheres to the surface of the lead film. I have found that though a thin layer of electrolytically deposited iron might be suitable so far as stripping is concerned, for use in the surface film, it is not desirable for ordinary purposes because of the fact that the copper deposit produced over it is uneven and irregular. This appears to be the result of the formation of sulphates of iron which are formed immediately upon contact of the iron film with the free acid in the electrolyte. This film of iron salts is powdery and does not adhere closely to the surface of the cathode. Also, it does not appear to be of uniform thickness in spots. When the deposition of copper occurs over the face of this film of iron salt the surface of the copper is irregular and pitted and when a very thin layer of electrolytic

copper is to be produced these irregularities are highly objectionable since they may interfere to such an extent as to make it impossible to produce a perfectly continuous layer of copper of the desired thickness. Zinc is also objectionable in this surface film, especially in copper deposition, and the results of these experiments have led me to conclude that the surface film should be applied to the cathode electrolytically and should be made of a metal which is substantially inert to the electrolyte from which the main deposit is to be made over the surface film, and which reacts with the electrolyte from which the main deposit is to be made, if at all, to produce a thin, continuous and uniform surface layer of the salt of the acid contained in that electrolyte.

While the process of electrodeposition which I have just described and which involves the electrolytic deposition of a surface film over the cathode applied to facilitate the stripping of the deposit, is of wide application, I have found that it is of particular importance in the production of starting sheets, such as are used in the electrolytic refining of copper. In one method of such refining, the crude metal as received from the smelter is cast in the form of anodes which are inserted in electrolytic cells. Thin starting sheets or cathodes are employed and the metal is deposited from the solution upon these starting sheets. When the deposit has built up to the desired extent, the starting sheet which is of refined copper, and the deposit formed thereon, are removed and may then be subjected to the other succeeding operations in the production of copper in its commercial forms, such as billets, bars, and the like. It is common practice, at present, to produce these starting sheets by making use of smooth copper blanks which are placed in electrolytic cells as cathodes. Deposition is carried on until the deposit has a weight of approximately one pound per square foot. Then the blank is removed and the deposit stripped from the surface thereof. This deposit is then used as the cathode in the main electrolytic cell and eventually passes through the successive commercial operations with the deposit formed thereon in that main cell. It is quite difficult to produce these thin starting sheets by the method described because of the difficulty of stripping them from the main blank, and while numerous schemes have been proposed for the purpose I have found that none of these suggested methods is wholly satisfactory. However, the method of the present invention overcomes the various difficulties heretofore present and the smooth copper blank is first treated with a thin layer of electrolytically deposited lead and then the starting sheet is deposited over the lead in

the usual way. The amount of lead which is employed in the film is so small that its presence is not harmful in the refining operations but on occasion it may be necessary to remove the adhering lead from the starting sheet after it has been stripped from the blank in order to insure that there is not sufficient lead remaining to interfere with the refining of the copper. This removal of the lead is a matter of no difficulty, however.

In addition to the application of the present invention to the production of starting sheets, it is of course useful for many other purposes. It may be used for the production of sheet copper either in the form of plain or corrugated sheets. These sheets may be of any desired size, depending, of course, on the size of the cathode which is used for the purpose. Instead of producing plain sheets, it is possible to produce sheets or plates with ornamental surfaces, such as are commonly used for building purposes. In producing such material the cathode will be suitably engraved or embossed, and the presence of the film of lead makes it possible to produce thin ornamental sheets, each of which is perfect and not disfigured by pin holes or tears. Because of the ease with which the deposited layer of copper may be removed from the cathode, it is possible to use this method in the production of metal foils which are of a much less thickness than anything that it has heretofore been thought possible to produce by electrolysis. Also, such foils may be produced at a cost which is far less than the cost of production by rolling methods. Other uses to which the process may be put are the production of radiators and tubes such, for instance, as are now used in automobiles, and the production of phonograph records. Another use of the invention is in the production of laminated gaskets and shims. A laminated metal product may be built up of alternate layers of lead and copper to any desired thickness, the copper enclosing and protecting the lead.

It will thus be seen that I have devised a process of electrodeposition and a cathode for use in that process, which makes it possible to produce metallic articles electrolytically of a thinness which was heretofore considered impossible. The additional step in the electrodeposition, involving the application of the metallic film to the cathode, is simple and much less expensive than numerous other expedients which have been suggested for the purpose of permitting the easy stripping of the deposit from the cathode. By the use of electrolytic methods, this surface film which facilitates stripping, may be produced without expensive equipment and since the film which is used is extremely thin the time involved in its application is very small.

I claim:

1. A process of electrodeposition which comprises electrolytically applying to the surface of a cathode blank, a thin film of metal, electrodepositing another metal over the film and then stripping off the deposit of the second metal while leaving the film in place on the surface of the blank.
2. A process of electrodeposition which comprises electrolytically applying to the surface of a cathode blank, a thin film of metal of comparatively little mechanical strength, electrodepositing over the film, another metal of greater mechanical strength, and then stripping off the deposit of the second metal while leaving the thin film in place on the surface of the cathode blank.
3. A process of electrodeposition which comprises applying to the surface of a cathode blank, a thin film of metal which is substantially inert to the electrolyte in the cell in which the cathode blank is to be used, electrodepositing over the film the metal from the said electrolyte and then stripping off the deposit while leaving the film in place on the cathode blank.
4. A process of electrodeposition which comprises applying to the surface of a cathode blank, a thin film of a metal which is not highly soluble in the electrolyte in the cell in which the cathode blank is to be used but which reacts therewith to produce a uniform closely adherent film of the salt of the metal, electrodepositing a layer of metal from the electrolyte over the film, and then stripping off the deposited layer while leaving the film in place on the surface of the cathode blank.
5. A process of electrodeposition which comprises electrodepositing over the surface of a cathode blank, a layer of a metal which is not highly soluble in the electrolyte in the cell in which the cathode blank is to be used but which reacts therewith to produce a uniform closely adherent film of the salt of the metal, electrodepositing a layer of metal from the electrolyte over the film and then stripping off the layer last deposited while leaving the layer first deposited in place on the surface of the blank.
6. A process of electrodeposition which comprises introducing a cathode blank into a cell containing in solution a metal which is substantially inert to the electrolyte in a cell in which the cathode is later to be used and depositing a thin film of the metal on the cathode, the solution containing the metal being one to which the material of the cathode blank is substantially inert, then inserting the coated cathode in the second cell, electrodepositing over the film a deposit of metal, and then stripping off the deposit while leaving the film in position on the cathode blank.
7. A process of electrodeposition which comprises applying to the surface of a cathode blank, a thin film of lead, electrodepositing another metal over the film, and then stripping the deposit from the surface of the film while leaving the latter in place.
8. A process of electrodeposition which comprises electrodepositing a thin film of lead over the surface of a cathode blank, electrodepositing another metal over the film, and then stripping this second deposit from the film while leaving the latter in place on the blank.
9. A process of electrodeposition which comprises applying to the surface of a cathode blank a thin film of lead, electrodepositing a layer of copper over the lead, and then stripping off the copper while leaving the latter in place.
10. A process of electrodeposition which comprises electrodepositing a thin film of lead over the surface of a cathode blank, electrodepositing a layer of copper from a copper sulphate solution over the lead film, and then stripping off the copper deposit while leaving the latter in place.
11. A process of electrodeposition which comprises applying to the surface of a cathode blank, a thin film of metal substantially inert to an electrolyte containing copper sulphate and free acid, electrodepositing copper from the electrolyte over the film, and then stripping off the deposited copper while leaving the film in place.
12. A process of electrodeposition which comprises electrodepositing over the surface of a cathode blank, a thin film of metal substantially inert to an electrolyte containing copper sulphate and free acid, electrodepositing copper from the electrolyte over the film, and then stripping off the deposited copper from the film while leaving the latter in place.
13. A process of electrodeposition which comprises inserting a cathode blank in a cell containing a solution of a lead salt, this solution being one to which the material of the blank is substantially inert, and in this cell, depositing a thin film of lead over the surface of the blank, electrodepositing copper upon the lead film, and then stripping the copper deposit from the surface of the lead film while leaving the latter in place.
14. A process of electrodeposition which comprises inserting a copper cathode blank in a cell containing a solution of lead silica fluoride, and in this cell depositing a film of lead on the blank, electrodepositing a layer of copper over the lead film, and then stripping the copper from the film of lead while leaving the latter in place.
15. A process of electrodeposition which comprises applying to the surface of a cathode blank, a thin film of metal, electrodepositing another metal over the film, and

then subjecting the blank and deposit to heat to facilitate the removal of the deposit from the film of metal.

16. A process of electrodeposition which comprises applying to the surface of a cathode blank, a thin film of metal, electrodepositing another metal over the film, and then subjecting the deposit and blank to the action of heat confined largely to the deposit to cause the latter to expand and free itself from the film.

17. A process of electrodeposition which comprises applying to the surface of a cathode blank, a thin film of metal having a comparatively low melting point, electrodepositing over the film a layer of metal having a higher melting point, and then subjecting the deposit and blank to the action of heat sufficient to cause the film to melt and free the deposit.

18. A process of electrodeposition which comprises applying to the surface of a cathode blank, a thin film of metal having a comparatively low melting point, electrodepositing over the film a layer of metal having a higher melting point and then passing an electric current through the film

and deposit to cause the film to soften and free the deposit.

19. A process of electrodeposition which comprises electrolytically applying to the surface of a cathode blank, a thin film of metal having a comparatively low melting point, electrodepositing over the film a layer of metal having a higher melting point, and then subjecting the blank and deposit to heat to facilitate the removal of the deposit from the film.

20. A cathode for use in the production of metal articles by electrolysis, these articles being stripped from the cathode, which comprises a body of electrically conducting material and a thin film of metal applied over the surface thereof, the metal in the film being substantially inert to the electrolyte from which the metal is to be deposited electrolytically upon the cathode.

21. A cathode for use in the production of metal articles by electrolysis, which comprises a body of electrical conducting material and a thin film of lead applied over the surface thereof.

In testimony whereof I affix my signature.
THOMAS ROBINSON.