

UNITED STATES PATENT OFFICE

2,583,100

TREATMENT OF A METALLIC CATHODE TO
RECEIVE ELECTRODEPOSITED METALHoward R. Wilson, Painesville, Ohio, assignor, by
mesne assignments, to Union Carbide and Car-
bon Corporation, a corporation of New YorkNo Drawing. Application March 25, 1947,
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2 Claims. (Cl. 204-112)

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This invention relates to the preparation of an iron cathode upon which iron is to be electrodeposited from an iron salt solution to the end that the deposited iron will adhere to the cathode with sufficient tenacity that the plate does not separate from the cathode in the plating tank nor as the plated cathode is removed from the tank but yet that the plate can easily be removed from the cathode by a minor mechanical operation, for instance by slightly prying the plate from the cathode or by vibrating or flexing the cathode. The present invention is useful in connection with the cathodes of the cell disclosed in the patent application of J. P. Oliver, filed March 25, 1947, Serial No. 736,939, for the recovery of iron from pickle liquor by the method disclosed in the patent application of Heise, Schumacher, and Wilson, filed March 25, 1947, Serial No. 737,000.

The present invention is to be differentiated from that art which is concerned principally with having the deposited metal adhere as permanently as possible to a cathode in the case where the cathode is a solid metal as, for instance, when a metallic object is given a protective coating.

In the recovery of iron from iron solutions it is desirable to deposit the iron on an iron cathode but to have the union of such a character that, although it introduces no appreciable electrical resistance into the system and is so firm that the cathode and plate do not separate in the cell and can be handled as a unit, the plate may easily be removed from the cathode when the unit is withdrawn from the cell. To be practical in commercial operations, whatever is done must be at a cost which is low in both time and materials.

In the recovery of iron by electrical deposition, it has been proposed to "blue" a starting sheet by heat treatment to produce a surface from which the electrodeposited iron can be separated, but this procedure is cumbersome, difficult to control and is costly in time, labor and required apparatus. It has also been proposed to receive deposited metal in a mercury cathode; but this requires a later separation of metal and mercury to recover the metal, e. g. a distillation of the amalgam or mixture.

It is now found that the desideratum may be accomplished quite simply by the proper treatment of an iron cathode with nitric acid.

To facilitate the action of the acid, the cathode is preferably cleaned before the acid treatment in order to remove dirt, grease and the like, which would prevent the acid from attacking the metal of the cathode at the desired areas. The

cleaning may be effected in any suitable manner as by washing or by an electrolytic treatment or by any method by which iron cathodes are usually cleaned, or dirt and grease are removed from a surface. Finally, the cathode is preferably washed with clean water just prior to the acid treatment.

Acid of substantially any strength may be used for treating the cathode but, in practice, it is preferred to use a fairly dilute aqueous solution of the acid, for instance from about a 5% to a 15% solution, to afford the operator time to treat the entire surface of the cathode which is to receive the plate without having the acid attack too much the portions of the cathode which are first treated. The acid may be applied to the cathode in any suitable manner as by spraying or the like, or by dipping the cathode in the solution. Dipping the iron cathode sheets in aqueous 10% HNO_3 causes brown fumes to appear in from about 10 to 25 seconds, which is a convenient length of time for the treatment. As soon as brown fumes appear from the major portion (or all) of the cathode sheet surface in the manner previously stated, the cathode is preferably flushed with clean water until no further fumes appear, and the cathode is then ready for use. It is important that the acid treatment not be prolonged as too long a treatment will give the surface a distinct etch which will not allow the iron plate easily to be removed. By the conditioning treatment, the surface of the cathode is somewhat roughened or etched, but very evenly if the cathode has properly been cleaned; and the surface has a matte finish but is free from surface pits. The preferred upper limit of acid treatment corresponds to 25 seconds immersion in a 10% HNO_3 solution; this does not etch the cathode so deeply but what the cathode may be given more acid treatments for successive uses without having the cathode etched so deeply that the plate is difficult to release. If the cathode is to be used once or only a very few times, the etching may be deeper.

The washed surface of the acid-treated iron cathode, treated only until the fumes appear, is slightly darkened by a slightly dark film which may be removed by scrubbing with a wet cloth and the surface appears to be etched only microscopically. Whether or not the dark film is present or has been scrubbed off, the treated surface readily receives from an iron sulphate or other suitable iron salt solution a good strike of deposited iron which, later, can easily be removed. It appears that by the acid treatment the iron

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surface is etched but, at least on the first acid treatment of the preferred minimum duration, so slightly that the etching is not visible to the naked eye and that a film containing iron combined with oxygen or nitrogen or both (a salt), is formed on the surface of the cathode and that both the very slight etching and the film, working together, give the results. The film which is useful may be the dark discoloration but the film which is in the incipient stage of formation is also operative as a good strike and a good strip can be obtained even though the discoloration is removed.

With the proper conditioning treatment the surface of an iron starting sheet is characterized by an even matte finish free from surface pits rather than a visible roughening or etching. If the surface shows to the naked eye a distinct crystalline etch, the treatment has gone too far, and the plated deposit cannot easily be removed. A properly conditioned surface may be used repeatedly without further treatment. However, a cathode may be given the acid treatment before each use, particularly if the surface has become oxidized when not in use. After the first treatment, succeeding treatments are preferably of minimum duration—the object being to restore the film but to etch the cathode as little as possible. The limit on the number of times that a cathode may be used depends upon the amount of etching. At each acid treatment, the surface of the cathode is etched to some extent and the points of etching may finally become so deep that the deposited iron does not easily release. Treating the cathodes only until the brown fumes appear (but no longer) etches the cathode to the minimum extent and allows it to be reused a greater number of times than if it is more deeply etched at each acid treatment. However, a deeply etched cathode may be reconditioned by shaving, grinding, sandblasting or the like to smooth the surface and then be used for another series of acid treatments and depositions. The advantage of the treatment described is its low cost, speed and simplicity and the effective results which may be obtained when properly operated; and, although the invention is of general application, it is of particular value in connection with a flexible cathode, for instance of sheet metal, so that the plate and cathode may easily be separated merely by flexing the cathode.

The invention is not limited to iron starting sheets. It has been found that good results can be obtained with such metals as copper, aluminum, Monel or stainless steel, although the treatment is not identical in all cases. With aluminum, Monel or stainless steel, for example, periods of as much as one hour in 10% acid may be required to give the desired surface; copper, on the other hand, behaves more like iron, requir-

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ing less than a minute in acid at room temperature. Room temperature (20–25° C.) is the most convenient temperature at which to treat the cathodes and is the preferred temperature, particularly with metals which are readily attacked by the acid as the action of the acid is slower the lower the temperature. With metals which are not readily attacked by the acid, more concentrated acid and higher temperatures may be used to shorten the time of treatment.

The invention is susceptible of modification within the scope of the appended claims.

What is claimed is:

1. In the art of winning iron from an aqueous solution of an iron salt by the electrodeposition of the iron from the salt onto an iron cathode, the method of conditioning the cathode prior to deposition of the iron which comprises subjecting the cathode to the action of aqueous nitric acid only until brown fumes appear from the cathode surface and the surface is given an evenly etched matte finish and presents a dark film, and then preventing further action of the acid, the surface being free of such distinct crystalline etch as to be visible to the naked eye and the amount of treatment corresponding to the immersion of the cathode in an aqueous 5% to 15% nitric acid solution for from 10 to 25 seconds.

2. Electrolytic method comprising electrolytically depositing iron on an iron cathode which has been subjected to the action of aqueous nitric acid only until brown fumes appear from the cathode surface and the surface presents a dark film, and then further action of the acid prevented; the cathode surface presenting an evenly etched matte finish free of such distinct crystalline etch as to be visible to the naked eye, the amount of treatment corresponding to the immersion of the cathode in an aqueous 5% to 15% nitric acid solution for from 10 to 25 seconds.

HOWARD R. WILSON.

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