Our invention relates to the plating of ferrous articles with zinc and more especially to the plating of such articles in relatively high acid solutions of zinc sulphate by means of currents of relatively high density delivered from anodes insoluble in such solutions, a principal object of the invention being to produce a zinc coating highly resistant to corrosion in the presence of weak acids of good appearance and wearing qualities, and which is tenaciously adherent to the ferrous base. Other objects of our invention are to provide a method by which zinc coatings of the character of those of which mention has been made can be economically and satisfactorily produced on ferrous articles in a commercial way; to provide a method of electroplating zinc on ferrous articles by means of which the evolution of hydrogen from the surface of the article, with the undesirable effects and results incident to such evolution, is substantially avoided or reduced to a negligible minimum and in which, during the plating operation, the amount of ferrous material dissolved from the article by the electrolyte is similarly reduced to a negligible minimum; and to provide a method which may be practiced by the use of electric currents which, while of relatively high density, that is, ampere per unit of cathode surface, are yet within limits permissible for satisfactory commercial operation and are utilized at good efficiency with corresponding decrease in production costs.

Other objects, advantages, novel features and characteristics comprehended by our invention are hereafter more specifically mentioned or will be apparent to those skilled in the art as a more detailed understanding of the invention is acquired from the following description.

In the performance of our invention we employ, as stated, acid solutions of zinc sulphate as the electrolyte and anodes of some material insoluble in such solution, for example, anodes of lead, the tanks or operating cells in which the operations are conducted being either lead lined or otherwise protected from the action of the solutions or else made of some material unaffected thereby. The article to be plated is employed as the cathode in the usual way and a direct current of suitable density arranged to flow thereto from the anodes, the zinc deposited on the article being thus abstracted from the electrolyte as the plating operation continues, so that to maintain the electrolyte at the predetermined or desired degree of acidity and to supply additional zinc to replace the zinc which has been plated out therefrom, fresh, preferably neutral, zinc sulphate solution must be supplied to the operating cells from time to time and a corresponding quantity of the spent electrolyte removed therefrom. This fresh neutral zinc sulphate solution may be obtained in any desired or convenient way, for example, by leaching zinc concentrates with the highly acid spent electrolyte and subjecting the resulting solution to suitable purification before its introduction to the operating cells or else by treating metallic zinc with the spent electrolyte or other acid solution.

It is well known that the deposition of zinc from highly acid zinc sulphate solutions on iron or steel articles acting as cathodes is first attended by the evolution and deposition of hydrogen at the cathode; this evolution of hydrogen materially diminishes the efficiency of the plating current and even under certain conditions quite effectively prevents the deposit of any material quantity of zinc at all. Additionally when a ferrous article is submerged in a highly acid solution of zinc sulphate the latter immediately attacks the article to an extent proportionate to the strength of the solution, so that a certain amount of the article may be dissolved before sufficient zinc can be de-
2 posited thereon to form a protective coating against the action of the solution.

Since the current density, that is amperage per unit of cathode surface, required to deposit a given coating from an acid solution of zinc sulphate varies almost directly with the acidity of the solution, it has heretofore been suggested that by using a current of very high density and an electrolyte of given acidity, a strike coating could be obtained satisfactorily in a very short interval of time with relatively little hydrogen evolution and that thereafter the plating of the article could be subsequently continued in a solution of greater acidity by the use of a current of lower density, and quite satisfactory results have been obtained in this manner, although the hydrogen evolution, while reduced, is still present in sufficient quantities to lower the current efficiency and to some extent affect the character of the plating. Particularly in this true if the surface being plated exhibits some irregularity because of pitting or the like.

We have found, however, that marked improvement in the character of the plating may be obtained and the evolution of hydrogen substantially negative or reduced to a negligible minimum, if the ferrous article be given a primary strike coating or plating in a solution of zinc sulphate of relatively low acidity by the use of a current of relatively high density for a short interval, and the then lightly zinc coated article then transferred to a bath of relatively higher acidity and the plating continued therein, initially by a current of still higher density so as to rapidly obtain a second strike coating of sufficient thickness to prevent the primary strike coating, which is partially soluble in the high acid bath, from being eaten away by the latter with resultant gas pitting and other irregularities in the subsequent deposit and thereafter, as soon as this second strike coating has been formed, by reducing the current to a density consonant with high efficiency and economy of operation and continuing the plating until an ultimate coating of the desired thickness is obtained.

In the preferred performance of our method, as briefly outlined in the preceding paragraph, we prefer to provide at least two and sometimes three plating tanks or operating cells and to transfer the article which is being plated from one cell to another as and when required. Thus in the first cell, we employ as the electrolyte an acid solution of zinc sulphate maintained at a relatively low acidity, for example, an acidity of 2% to 2½% i.e. containing 20 to 25 grammes H₂SO₄ per litre of solution, while in the second and subsequent operating cells, if any, a similar electrolyte of higher acidity, for example from 4% to 5% although higher or lower acidities are permissible and will under some conditions be found desirable. A small quantity of a suitable addition agent may be added to the solution in each cell, if desired, and will frequently be found beneficial.

Each cell is provided with one or more anodes of lead or other material insoluble in the electrolyte and suitable connections are arranged for causing a direct current to flow therefrom through the electrolyte to the article to be plated which acts as a cathode in the usual way.

For the most satisfactory results it is requisite that the ferrous article to which the zinc coating is to be applied be given a suitable surface conditioning before its introduction to the first operating cell. This conditioning may consist of immersion in an alkali cleaning solution to effect grease removal, followed by rinsing and pickling to remove scale, again followed by rinsing or brushing and rinsing. The article may then preferably be immersed in a weak solution of nitric acid, that is, a solution containing 10% or less per volume of acid, for a short interval, say about 30 seconds, and again rinsed in water; further reference will hereinafter be made to the purpose and desirability of this operation. We also consider it advisable to vigorously brush the article after the final washing while frequently a similar brushing before the final washing will be found advantageous.

The article having thus been rendered properly zinc-receptive by the conditioning operations to which we have referred or others of corresponding efficacy, is now ready for introduction to the first operating cell to effect the primary strike coating by the passage through the cell for an interval of one or two minutes or thereabouts of a current of approximately 100 amperes per square foot of article or cathode surface. Because of the relatively low acidity of the electrolyte in this cell in comparison with that of the subsequent cell or cells, there is little or no hydrogen evolution during the deposition of this primary coating and the same is therefore formed smoothly and evenly over the article in a relatively short time and at relatively good current efficiency, the coating, however, being somewhat softer and less resistant than coatings formed in more highly acid solutions. Additionally, because of the relatively low acidity of the electrolyte the ferrous article is attacked but very slightly thereby during the very short interval it is submerged therein before it is covered, or at least partially covered, with the zinc so that no appreciable pitting or dissolving away of the surface of the article occurs.

The primary zinc strike coating having thus been formed on the article in the first cell, the current is shut off and the article immediately transferred to the second operating cell which, as hitherto stated, contains
an electrotype of appreciably higher acidity and thus capable, at least to some extent, of dissolving the relatively soft primary strike coating and in turn attacking the ferrous base. To prevent this result, as soon as the article is immersed in the electrolyte, a second coating is somewhat accelerated by passing a direct current of very high density through the cell, for example, a current having a density of approximately 150 amperes per square foot of article surface, for sufficient time, ordinarily about two minutes under the conditions stated, to thoroughly coat the article with the harder zinc deposit obtainable in the presence of the high acid solution. The formation of this second strike coating, however, is not attended with a material evolution of hydrogen because of the presence of the primary zinc coating upon the article which not only facilitates the deposit of the zinc but prevents the hydrogen evolution which would occur in its absence with corresponding enhancement of the current efficiency but also prevents the high acid electrolyte from injuriously attacking the ferrous base.

While under certain conditions it is feasible to continue the plating operation with the very high density current utilized for the formation of the second strike coating until an ultimate deposit of the desired thickness is obtained, the use of currents of such character for material periods of time such as required to complete the plating operation is uneconomical both from the standpoint of current efficiency and also because of the difficulties inherent in the transport and handling of such currents, the installation cost of the busbars and other connections and instrumentalities required therefor and the correspondingly great maintenance expense. Therefore in accordance with the preferred practice of our invention, as soon as the second strike coating has been formed the current flowing through the cell is materially reduced, say to a density of about 100 amperes per square foot of article surface, and the plating operation then continued with this relatively lower current until an ultimate coating of the desired thickness is obtained. This final plating operation may be carried out in the second operating cell, or after the second strike coating has been formed therein, the current may be shut off entirely and the article transferred to a third operating cell desirably containing an electrolyte of substantially similar acidity as that in the second cell and the plating completed in this third cell by the use of the lower density current as above described. However, irrespective of which method may be adopted under practical conditions, it is apparent that as the extremely high density current is utilized in the formation of the second strike coating for but a relatively short interval it is unnecessary to provide instrumentalities and connections for handling the same of as great size and capacity as would be required if the current were employed for a longer period so that both initial installation and upkeep cost are materially reduced from what they would otherwise be, while as the second strike coating when deposited is extremely receptive to the deposition of the zinc during the subsequent plating and by its complete coverage of the ferrous base prevents any appreciable hydrogen evolution, the relatively lower current thereafter employed operates at equal or even better efficiency than the current used for the second strike coating with resultant economy in production costs.

After the ultimate coating is obtained the article, which may be a sheet, pipe, bar, or in fact any other sort or kind of article, is removed from the tank, rinsed, and brushed if desired, and is then ready for the market.

Mention has heretofore been made of the desirability of immersing the article before its introduction to the bath in the first operating cell in a weak solution of nitric acid and this step we therefore prefer to employ where possible as we have found that by so doing, particularly in the case of articles having slightly uneven or irregular surfaces or those in which the surface has been cut into by threading or other machining operations, the tendency to "gas pit" during the subsequent plating operations is materially reduced. Additionally we have found that if during the said operations the article be more or less gently tapped with a wooden bar or the like at intervals of 15 seconds or thereabouts the tendency to formation of and adherence of gas bubbles with resulting gas pitting is likewise reduced, and therefore, with a view to substantially eliminating all gas pits or similar imperfections we prefer to employ the nitric acid treatment and also to tap the article or otherwise slightly agitate it at intervals during the plating operations.

By the practice of our improved method of electroplating ferrous articles with zinc, we are able to produce upon such articles zinc coatings which are more perfect in appearance, more resistant to corrosion in the presence of weak acids and which otherwise respond to the Pierce and other commercial tests ordinarily employed in testing zinc coatings on ferrous articles more satisfactorily than any other zinc coatings or platings on articles of like character which, so far as we are advised, it has been possible to produce by any of the methods heretofore employed, and which may be generally characterized as hot dipping processes in which the article to be coated is dipped after suitable preparation in the bath of molten spelter or processes in which the coating is formed by electroplating.
ing. While of course the attainment of this end constitutes the primary object of our invention, the fact that our method may be practiced in a commercially satisfactory way both as to initial installation and upkeep costs, simplicity of procedure, high current efficiency and consequent economy renders it extremely desirable from a practical operating standpoint and we therefore believe that it constitutes a distinct contribution to the art.

While we have herein described one manner of practicing our invention with considerable particularity, we do not thereby desire or intend to specifically confine or limit ourselves thereto as variations and modifications may be made therein particularly with respect to the acidities of the electrolytes in the different cells, in the densities of the various currents employed and in the periods in which they are permitted to flow, in accordance with the particular results desired or the particular operating conditions encountered, without departing from the spirit and scope of the invention as defined in the appended claims.

Having thus described our invention we claim and desire to protect by Letters Patent of the United States:

1. The method of electroplating zinc on ferrous articles which comprises the steps of first forming on the article a primary strike coating of zinc by immersing the article in a bath of zinc sulphate solution containing substantially 2% sulphuric acid and passing therethrough from an anode insoluble in such solution to the article a current having a density of approximately 100 amperes per square foot of article surface, and then transferring the article to another bath of zinc sulphate solution, containing substantially 5% sulphuric acid and continuing the plating therein by passing to the article a current having a density of approximately 150 amperes per square foot of article surface to form a second strike coating thereon.

2. The method of electroplating zinc on ferrous articles which comprises the steps of first forming on the article a primary strike coating of zinc by immersing the article in a bath of zinc sulphate solution containing substantially 2% sulphuric acid and passing therethrough from an anode insoluble in such solution to the article a current having a density of approximately 100 amperes per square foot of article surface, and then transferring the article to another bath of zinc sulphate solution containing substantially 5% sulphuric acid and continuing the plating therein by passing to the article from an anode insoluble in such solution a current having a density of approximately 150 amperes per square foot of article surface to form a second strike coating thereon.

3. The method of electroplating zinc on ferrous articles which comprises the steps of first forming on the article a primary strike coating of zinc by immersing the article in a bath of zinc sulphate solution containing substantially 2% sulphuric acid and passing therethrough to the article a current having a density of approximately 100 amperes per square foot of article surface, and then transferring the article to another bath of zinc sulphate solution containing substantially 5% sulphuric acid and continuing the plating therein by passing to the article a current having a density of approximately 150 amperes per square foot of article surface to form a second strike coating thereon.

4. The method of electroplating zinc on ferrous articles which comprises the steps of first forming on the article a primary strike coating of zinc by immersing the article in a bath of zinc sulphate solution containing substantially 2% sulphuric acid and passing therethrough from an anode insoluble in such solution to the article a current having a density of approximately 100 amperes per square foot of article surface, and then transferring the article to another bath of zinc sulphate solution containing substantially 5% sulphuric acid and continuing the plating therein by passing to the article from an anode insoluble in such solution a current having a density of approximately 150 amperes per square foot of article surface to form a second strike coating thereon.

5. The method of electroplating zinc on ferrous articles which comprises the steps of first forming on the article a primary strike coating of zinc by immersing the article in a bath of zinc sulphate solution containing substantially 2% sulphuric acid and passing therethrough to the article a current having a density of approximately 100 amperes per square foot of article surface, and then transferring the article to another bath of zinc sulphate solution containing substantially 5% sulphuric acid and continuing the plating therein by passing to the article a current having a density of approximately 150 amperes per square foot of article surface to form a second strike coating thereon.

6. The method of electroplating zinc on ferrous articles which comprises the steps of first forming on the article a primary strike coating of zinc by immersing the article in a bath of zinc sulphate solution containing substantially 2% sulphuric acid and passing therethrough to the article a current having a density of approximately 100 amperes per square foot of article surface, and then transferring the article to another bath of zinc sulphate solution containing substantially 5% sulphuric acid and continuing the plating therein by passing to the article from an anode insoluble in such solution a current having a density of approximately 150 amperes per square foot of article surface to form a second strike coating thereon and finally reducing the current to approximately 100 am-
peres per square foot of article surface and continuing the plating operation until a coating of predetermined thickness is obtained. In witness whereof we have affixed our signatures.

SIDNEY H. DAVIS.
CARL O. ANDERSON.
RUDOLPH J. STENGL.
WILLIAM N. SMITH.
HERBERT R. HANLEY.