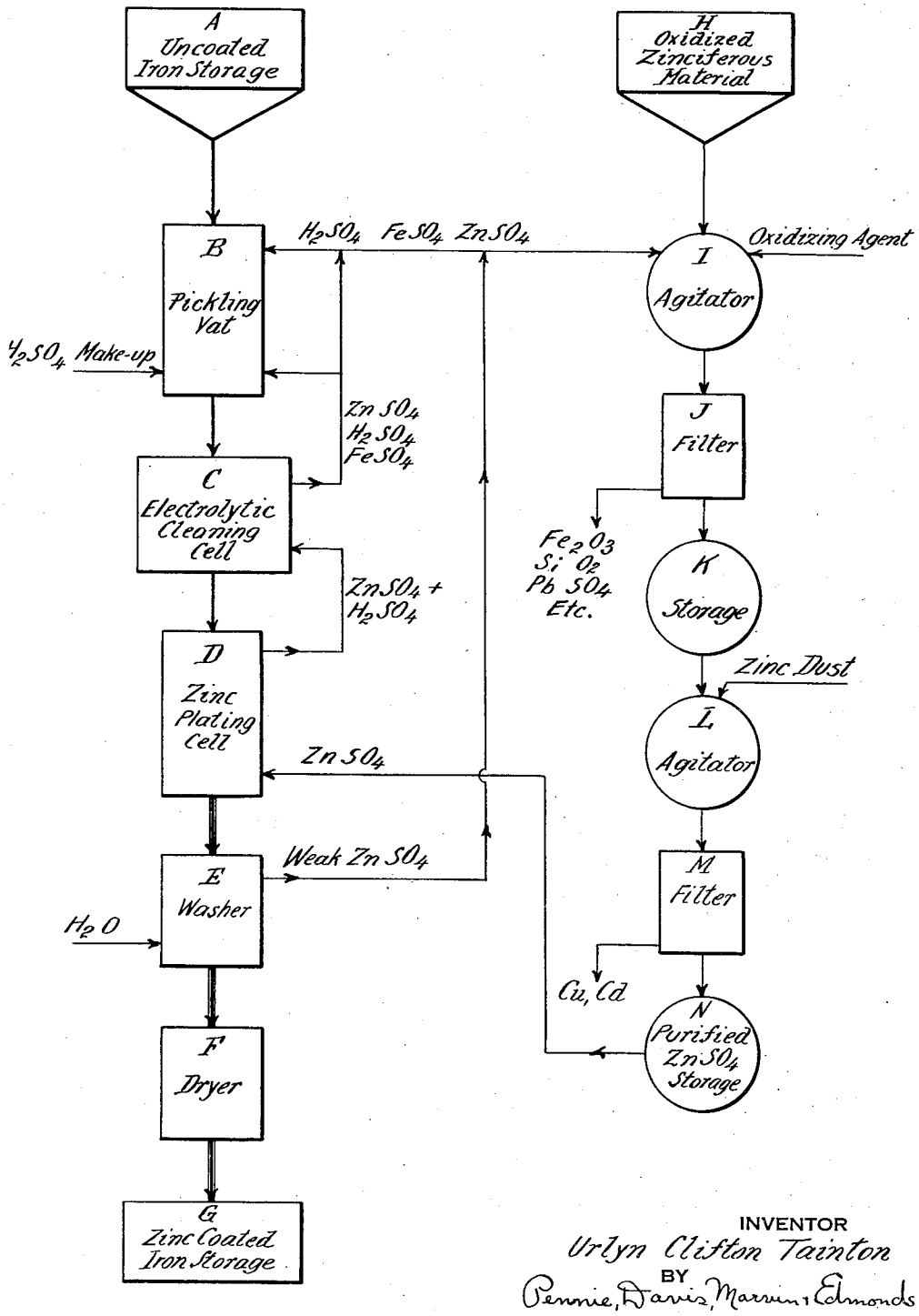
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COATING FERROUS ARTICLES WITH ZINC

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COATING FERROUS ARTICLES WITH ZINC

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This invention relates to the coating of ferrous articles with zinc by electrodeposition. Broadly, the object of the invention is to provide an improved method of coating iron, steel and similar ferrous articles with zinc by electrodeposition, sometimes called electro-galvanizing. Thus, the invention aims to provide a method of electrodepositing zinc upon ferrous articles from which there results a more adherent and physically superior zinc coating than obtainable by the heretofore customary zinc coating practices. Another object of the invention is to provide an improved method of preparing the ferrous article for the reception of the zinc coating. In particular, the invention aims to provide an improved method of coating ferrous articles with zinc by electrodeposition at a relatively high current density with insoluble anodes from a zinc electrolyte of relatively high free acid content.

Of the many forms of protection that have been used for the preservation of iron surfaces, none is so satisfactory in point of permanence and economy as that afforded by a layer of zinc. Preparatory to coating a ferrous article with zinc, it is necessary that its surface be thoroughly cleaned and freed from rust, scale, etc. This is ordinarily accomplished by immersing the article to be zinc-coated in a pickling solution consisting of dilute hydrochloric or sulphuric acid. During the pickling operation the acid becomes progressively weaker owing to the solution of iron and iron oxides, and eventually has to be discarded. Many thousands of tons of acid are used annually for this purpose in the galvanizing industry. This of course represents a considerable item of expense. Further, the disposal of the spent pickling acid often presents a serious industrial problem.

After the surface of the ferrous article has been appropriately cleaned, it is subjected to the galvanizing or zinc-coating operation. At the present time, by far the most important method of zinc coating (in point of volume of production) is the so-called "hot-dip" process in which the article is immersed in a bath of molten zinc. The zinc coating so obtained, however, suffers from several serious disabilities, notably poor adhesion to the metal base, irregularity in thickness and contamination with iron. For certain special work, therefore, the hot-dip process has been replaced, to a small extent, by zinc electrodeposition (generally known as electro-galvanizing) in which the ferrous article is made cathode in an electrolytic cell having anodes of metallic zinc and an electrolyte of zinc cyanide, sodium zincate or neutral zinc sulphate.

In accordance with the present invention, the ferrous article is coated with zinc by electrodeposition at a relatively high current density with insoluble anodes in a strongly acid zinc electrolyte. The electrodeposition is continued until an appropriate part of the zinc has been extracted from the electrolyte, with simultaneous regeneration of acid. One of the important features of the invention involves the use of the strongly acid spent electrolyte to effect the pickling or cleaning of the ferrous article with accompanying solution of iron in the form of ferrous and/or ferric salts. The spent cleaning liquor together with spent electrolyte (not used in the cleaning operation) are then treated with zinciferous material to regenerate the zinc electrolyte. The regenerating operation includes precipitation of iron, preferably by oxidation, and the elimination of other contaminants to provide the purified zinc electrolyte required for electrodeposition. Since it is now my preferred practice to use an electrolyte made up of zinc sulphate and free sulphuric acid, the invention will be hereinafter described with particular reference to such an electrolyte, although it is to be understood that other zinc salts and other acids may be used in making up the electrolyte.

I have used with advantage in zinc-coating ferrous articles by electrodeposition an electrolyte containing about 200 to 300 grams per liter of free sulphuric acid and 50 to 70 grams of zinc per liter in the form of sulphate. In any case, the electrolyte should contain at least 10% of free acid, and preferably 20% or more. The electrodeposition is conducted with a current density of at least 50 amperes per square foot, and preferably 400 to 600 amperes per square foot. The spent electrolyte will contain 20% or more of free sulphuric acid. In regenerating the spent electrolyte (together with such portion thereof as is diverted to the cleaning operation), the excess acid is neutralized by the addition of material containing zinc in the form, for example, of oxide or carbonate. Suitable zinciferous material for the purpose comprises roasted zinc concentrates, finely divided oxidized zinc ores, refuse zinc oxide etc. The iron present in the liquor (as a consequence of the cleaning operation) is previously or simultaneously oxidized to the ferric form by means of a suitable oxidizing agent such as manganese dioxide, potassium permanganate or the like. Continued addition of zinc oxide then re-

sults in a reaction with ferric sulphate as follows:

$$Fe_2(SO_4)_3+3ZnO=3ZnSO_4+Fe_2O_3.$$

The sulphate from the sulphuric acid which has combined with the iron in the pickling operation is thus converted to zinc sulphate while the iron is precipitated as ferric oxide together with any insoluble material that may have been added along with the zinc oxide. The solution is then separated from this insoluble residue and is purified, if necessary, for the removal of other metals such as copper, cadmium, etc., by treatment with metallic zinc, preferably in the form of zinc dust. All metals below zinc in the electro-chemical scale are thus precipitated and may be removed by filtration or otherwise, yielding a solution of practically pure zinc sulphate.

The regenerated and purified zinc sulphate solution (appropriately adjusted as to its free acid content, by the addition of sulphuric acid if necessary) is added at a carefully controlled rate to the electrolytic cells in which the electrodepositing operation is being conducted. This operation results in the deposition of metallic zinc on the ferrous articles to be coated and the regeneration of sulphuric acid, including that consumed in the pickling or cleaning operation.

The improved electrodeposition process of the invention permits the use of zinc ores and other relatively inexpensive zinciferous materials as the immediate source of zinc for the zinc-coating operation, in contrast to the use of high grade zinc metal heretofore employed in both the hot-dip process and electro-galvanizing with zinc anodes. Furthermore, the cost of the acid heretofore used for pickling is eliminated, since in the process of the invention substantially all of the acid consumed in cleaning the ferrous articles is ultimately set free in the electrolytic cells.

Instead of employing spent electrolyte as a simple pickling liquor, I find it often advantageous to supplement the chemical cleaning action of the acid liquor by an electrolytic action. Thus, the ferrous article (preferably after simple immersion in the strongly acid spent electrolyte) may be made either the anode or the cathode, or both successively, in an electrolytic cell with spent zinc electrolyte. Where the ferrous article is made the cathode in this electrolytic cleaning action, the applied current density should be kept down below the point at which the over-voltage of hydrogen exceeds the zinc potential. In other words, below the point at which zinc begins to plate out from the strongly acid solution. By so doing hydrogen is evolved at the surface of the article and the cleaning effect of the acid is thereby enhanced.

Especially good results, particularly as regards the bond between the zinc coating and the surface of the ferrous article, are obtained by making the article anode in the electrolyte immediately prior to its reception of the zinc coating, as more particularly described and claimed in the companion application of myself and Frank W. Harris, Serial No. 597,622; filed March 8, 1932. By suitable electric connections this may be conveniently and advantageously carried out in the same electrolytic cell in which the electrodeposition of zinc is carried out. Care should be exercised to prevent the iron content of the electrolyte reaching a concentration high enough to interfere with the production of a good coating of zinc.

Instead of using spent electrolyte for the pickling or cleaning operation, it may sometimes be of advantage to employ sulphuric acid, more or less free from zinc, as the pickling liquor and/or as the electrolyte in the electrolytic cleaning action, and to return the ferrous sulphate entering into solution therein to the zinc leaching circuit where it is subjected to the regeneration operation hereinbefore described. Such fresh amounts of sulphuric acid as are necessary to compensate for the inevitable losses in the cyclic operation may be added to the cleaning liquor, or during the regeneration operation, or to the purified zinc electrolyte.

In the single figure of the accompanying drawing, there is diagrammatically represented a flow-sheet of a cyclic operation embodying the invention in what I now consider its preferred form. As a specific illustration of the manner of practicing the invention, its application to the zinc-coating of steel wire will be described by reference to the drawing. The uncoated steel wire is delivered from a storage unit A to a pickling or cleaning vat B. This vat may contain either sulphuric acid or spent electrolyte from the electrolytic cells containing, say, 50 grams per liter of zinc and, say, 300 grams per liter of sulphuric acid. After preliminary cleaning in the vat B, the wire proceeds to an electrolytic cleaning cell C where it is subjected to electrolytic action, either anodic or cathodic, as desired. If cathodic, the current density is held down to a point such that zinc will not plate out on the steel. Where an anodic cleaning action is utilized, the current density is not limited by this consideration. Instead of carrying out this electrolytic cleaning operation in a separate cell, it may readily be arranged that the cleaning cell is a part of the cell used for the actual plating of the zinc. This may be accomplished, in the case of cathodic cleaning, by appropriately disposing the anodes to give the proper current density, or, in the case of anodic cleaning, by passing the wire through a transverse partition in the cell and so disposing the electrodes that as the wire passes through this partition it changes from anodic to cathodic potential. In the treatment of individual objects which are not passed continuously through the cell, the applied voltage may be varied at the commencement of the electrolytic action so as to give the proper kind and intensity of current suitable for optimum cleaning results.

The wire, following the cleaning operation, passes through a zinc plating cell D where the electrodeposition of zinc is carried out. Preferably, the zinc electrolyte in this cell contains a high percentage of free acid, for example, 15% or more, and a relatively high cathodic current density is used. Thus, an electric current of several hundred amperes (e. g. 500 amperes) per square foot of cathode surface may be advantageously and successfully employed. After subjection to electrodeposition for a sufficient time interval to receive a suitable deposit of zinc, the resulting zinc-coated wire leaves the cell D and is washed with water in a vat E to free it from adhering salts and acid. The wire then passes through a drying apparatus F, such as a steam-heated pan filled with sawdust or similar material. The wire is then wound on a reel and goes to the zinc-coated or galvanized wire storage G.

The spent electrolyte from the zinc plating cell D, which may contain as much as 30% or more of free sulphuric acid, is conducted, in whole or in part, to the electrolytic cleaning cell C. Here the appropriate current is applied and a certain amount of iron is taken into solution.

The liquor discharged from the cell C may be taken directly to the first stage of the regeneration operation or may be conducted, in whole or in part, to the pickling vat B. Alternatively, fresh sulphuric acid may be added to the vat B. In any event, the spent cleaning liquor from the vat B with its iron sulphate content is conducted to the first step of the regeneration operation along with such amounts of spent electrolyte, from the cells C and D, as are not diverted to the cleaning operation.

The liquor delivered to the regeneration operation accordingly comprises a mixture of sulphuric acid, residual zinc sulphate and iron sulphate. The iron in this liquor is oxidized by treatment in an agitator I with permanganate or manganese dioxide, whereby ferrous sulphate is oxidized to ferric sulphate. Oxidized zinciferous material, such as roasted zinc ore, from a bin H is then added to the liquor to neutralize the acid and form zinc sulphate. After the strength of the acid is sufficiently reduced (preferably not below 10 to 20% of free acid), the continued addition of zinc oxide results in a reaction with the ferric sulphate, precipitating hydrated ferric oxide and yielding zinc sulphate in solution. The iron sulphate in the liquor delivered to the regeneration operation performs a very useful function. During and following the precipitation of the hydrated ferric oxide the arsenic and antimony which have been taken into solution from the zinc ore is precipitated, forming various insoluble compounds with the precipitated iron compounds.

The mixture of zinc sulphate solution and ferric hydrate, together with other material such as silica, lead sulphate, etc., which may have been added along with the roasted zinc ore, is then filtered in an appropriate apparatus J. The solids resulting from the filtering operation may be treated for the extraction of lead and such other values as they may contain, and the filtrate is delivered to a storage vat K. In the ordinary course of operations this filtrate may and usually will contain, in addition to zinc sulphate, a certain amount of other metals (as sulphates) such as cadmium, copper and the like. Such other metals are precipitated by agitation with zinc dust in an agitator L, thus bringing about the elimination of metals below zinc in the electro-chemical scale. The resulting mixture from the agitator L is passed through a filter M and the filtrate is delivered to a storage tank N for purified zinc electrolyte. The residues from the filter M, consisting of copper, cadmium, etc., may be appropriately treated for the recovery of their values.

The purified zinc electrolyte is conducted from the storage tank N to the electrolytic cell D at a carefully controlled rate, as required in order to maintain the zinc and acid concentrations of the electrolyte in the cell within the contemplated limits. The spent electrolyte passes on to the cleaning operation and back to the regeneration operation in another cycle.

It will be clear from the foregoing description that in the process of the invention there is no discarding of the spent pickling acid. Such iron as enters solution in the pickling operation is removed from solution in the form of precipitated ferric oxide, and the sulphate radical (combined with the iron while in solution) is made to combine with zinc and is ultimately set free again in the form of sulphuric acid in the electrodepositing operation. Further, by the practice of the invention, relatively cheap sources of raw zinc material are directly available for zinc coating, in place of high grade zinc metal heretofore customarily used in galvanizing. Electrodeposition at relatively high current densities with a strongly acid zinc electrolyte insures rapid coating in addition to the economies in acid consumption hereinbefore mentioned. Moreover, the zinc coated article, resulting from the practice of the invention, is a superior product, notably in the uniformity of the zinc coating and its adherence to the surface of the ferrous article.

Pickling or cleaning of the ferrous article in an acid liquor made up in large part of spent electrolyte has a further advantage due to the presence of the zinc salt. Thus, I have found that the presence of the zinc salt in the pickling liquor acts as an inhibitor of the action of the acid on the metallic iron, without objectionably impairing the action of the liquor as an effective pickling agent. In general, the inclusion in the pickling liquor containing 10% or more free acid of a substantial amount of zinc salt of the same acid improves the pickling liquor particularly by minimizing the solution of iron.

In certain respects, the present invention is an improvement upon the process of coating ferrous articles with zinc by electrodeposition described in my United States Patents Nos. 1,210,017, December 26, 1916 and No. 1,247,179, November 20, 1927.

I claim:—

1. The process of coating ferrous articles with zinc by electrodeposition, which comprises subjecting the article to a cleaning operation with an acid liquor in the course of which some iron goes into solution in the liquor, conducting the spent cleaning liquor and the spent electrolyte from the electrodepositing operation to a regenerating operation where the combined liquors are treated with zinciferous material to regenerate the zinc electrolyte, the regenerating operation including precipitation of iron and appropriate purification of the regenerated electrolyte, and subjecting the cleaned article to electrodeposition with the regenerated zinc electrolyte and insoluble anodes in the course of which acid is regenerated for return to the cleaning operation.

2. The process of coating ferrous articles with zinc by electrodeposition, which comprises subjecting the article to a cleaning operation with an acid liquor in the course of which some iron goes into solution in the liquor, conducting the spent cleaning liquor and the spent electrolyte from the electrodepositing operation to a regenerating operation where the combined liquors are treated with zinciferous material under oxidizing conditions to precipitate iron and regenerate the zinc electrolyte, and subjecting the cleaned article to electrodeposition with the regenerated zinc electrolyte and insoluble anodes in the course of which acid is regenerated for return to the cleaning operation.

3. The process of coating ferrous articles with zinc by electrodeposition, which comprises cleaning the article with sulphuric acid with accompanying production of iron sulphate, conducting the spent cleaning liquor and the spent electrolyte from the electrodepositing operation to a regenerating operation where the combined liquors are treated with zinciferous material to form zinc sulphate for regeneration of the electrolyte, the regenerating operation including precipitation of iron and appropriate purification of the regenerated electrolyte, and subjecting

the cleaned article to electrodeposition with the regenerated zinc electrolyte and insoluble anodes in the course of which sulphuric acid is regenerated for return to the cleaning operation.

4. The process of coating ferrous articles with zinc by electrodeposition, which comprises cleaning the article with sulphuric acid with accompanying production of iron sulphate, conducting the spent cleaning liquor and the spent electrolyte from the electrodepositing operation to a regenerating operation where the combined liquors are treated with zinciferous material under oxidizing conditions to precipitate iron and to form zinc sulphate for regeneration of the electrolyte, and subjecting the cleaned article to electrodeposition with the regenerated zinc electrolyte and insoluble anodes in the course of which sulphuric acid is regenerated for return to the cleaning operation.

5. The process of coating ferrous articles with zinc by electrodeposition, which comprises subjecting the article to a cleaning operation with an acid liquor in the course of which some iron goes into solution in the liquor, subjecting the cleaned article to electrodeposition at a relatively high current density with insoluble anodes in a zinc electrolyte relatively high in free acid, and conducting the spent cleaning liquor and the spent electrolyte to a regenerating operation where the combined liquors are treated with zinciferous material to regenerate the zinc electrolyte, the regenerating operation including precipitation of iron and appropriate purification of the regenerated electrolyte.

6. The process of coating ferrous articles with zinc by electrodeposition, which comprises subjecting the article to a cleaning operation with an acid liquor in the course of which some iron goes into solution in the liquor, subjecting the cleaned article to electrodeposition at a relatively high current density with insoluble anodes in a zinc electrolyte relatively high in free acid, and conducting the spent cleaning liquor and the spent electrolyte to a regenerating operation where the combined liquors are treated with zinciferous material under oxidizing conditions to precipitate iron and regenerate the zinc electrolyte.

7. The process of coating ferrous articles with zinc by electrodeposition, which comprises subjecting the article to a cleaning operation with spent electrolyte from the electrodepositing operation containing a relatively high percentage of free sulphuric acid, conducting the spent cleaning liquor to a regenerating operation where the liquor is treated with zinciferous material to regenerate the zinc sulphate electrolyte, and subjecting the cleaned article to electrodeposition with insoluble anodes in the regenerated electrolyte.

8. The process of coating ferrous articles with zinc by electrodeposition, which comprises subjecting the article to a cleaning operation with spent electrolyte from the electrodepositing operation containing a relatively high percentage of free acid, subjecting the cleaned article to electrodeposition at a relatively high current density with insoluble anodes in a zinc electrolyte relatively high in free acid, and treating the spent cleaning liquor with zinciferous material to regenerate the zinc electrolyte.

9. The process of coating ferrous articles with zinc by electrodeposition, which comprises subjecting the article to an electrolytic cleaning operation with spent electrolyte from the electrodepositing operation, subjecting the cleaned article to electrodeposition at a relatively high current density with insoluble anodes in a zinc electrolyte relatively high in free acid, and treating the spent liquor from the electrolytic cleaning operation with zinciferous material to produce zinc electrolyte for the electrodepositing operation.

10. The process of coating ferrous articles with zinc by electrodeposition, which comprises subjecting the article to a cleaning operation with spent electrolyte from the electrodepositing operation, treating the spent cleaning liquor with zinciferous material to produce zinc electrolyte for the electrodepositing operation, and subjecting the cleaned article to electrodeposition with insoluble anodes in a zinc electrolyte relatively high in free acid.

11. The process of coating ferrous articles with zinc by electrodeposition, which comprises subjecting the article to a cleaning operation with spent zinc sulphate electrolyte from the electrodepositing operation, treating the spent cleaning liquor with zinciferous material to form zinc sulphate for regeneration of the electrolyte, and subjecting the cleaned article to electrodeposition at a relatively high current density with insoluble anodes in a zinc sulphate electrolyte relatively high in sulphuric acid.

12. The process of coating ferrous articles with zinc by electrodeposition, which comprises subjecting the article to a cleaning operation with spent electrolyte from the electrodepositing operation in the course of which some iron goes into solution, treating the spent cleaning liquor with zinciferous material under oxidizing conditions to precipitate iron and regenerate a zinc electrolyte, and subjecting the cleaned article to electrodeposition at a current density of 50 or more amperes per square foot with insoluble anodes in the regenerated and appropriately purified zinc electrolyte having a free acid content of 10% or more.

13. A cyclic process for coating ferrous articles with zinc, comprising the steps of subjecting the ferrous articles to electrodeposition at a relatively high current density with insoluble anodes in a zinc salt containing electrolyte relatively high in free acid, using spent electrolyte from the zinc depositing operation for cleaning the uncoated ferrous articles, regenerating the spent cleaning solution to receive the electrolyte for the zinc depositing operation, and utilizing the regenerated electrolyte for depositing zinc upon the cleaned ferrous articles.

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