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METHOD OF ETCHING STEEL

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This invention relates to a new method of treating steel or metal objects subsequent to the pickling operation and has particular relation to a method whereby steel sheets, strips, tubes, pipe or wire can be rapidly etched either continuously or by a batch process.

One of the principal objects of this invention is to provide a method for etching steels which is simple and easy to carry out, which will greatly reduce the time required for this operation, and which permits the operator to obtain a uniform etch on succeeding sheets without resorting to calculation or guess.

Other objects will be apparent from the following description.

In the manufacture of galvanized steel sheets, the sheet steel coming from the rolling mill operations is pickled in sulfuric acid to remove and loosen the oxide scale or rust which has formed on the steel surfaces. The sheets are washed in water to remove the acid, neutralized in alkaline solutions and are then transferred to the galvanizing process. The sheets pass through muriatic acid which acts as a flux directly into the fluxing chamber of the galvanizing pot and then through the molten metal. The coated sheets are cooled after which they are ready for further treatment.

The usual method of pickling sheets of steel which are not to be coated with a protective metal such as zinc, is to place them in 5 to 8% sulfuric acid solutions at elevated temperatures for from 20 to 60 minutes. An inhibitor is often added to the sulfuric acid bath and results in savings of both acid and steel by slowing up the reaction of the acid on the steel surface without affecting the reaction of the acid with the scale or rust. When the steel is to be galvanized in a later operation it is not usually possible to use an inhibitor without affecting adversely the adhesion of the coating and hence the shape and size of the "spangle" on the coated sheets. In the case of galvanizing, the steel sheets are pickled and etched by treatment for 30 to 90 minutes at elevated temperatures in 6–8% sulfuric acid solutions. The time of treatment depends on the type of steel, amount of scale present and on the kind of coating which is to be applied to the steel. Thus in the case of zinc coatings, an ordinary commercial coat can be applied to the steel after a comparatively short pickle or etch, whereas when a tight coat, which will not crack or flake on bending, is desired, a longer time of treatment is necessary.

It has been found that by the use of ferric sulfate as an etching agent it is possible to use steel previously pickled with inhibited sulfuric acid and still apply a good commercial coating of zinc thereon. Moreover, when a ferric sulfate etch is employed an excellent, tight coating may be put on the steel in the galvanizing bath. This invention provides a method for applying this ferric sulfate etch quickly and uniformly so that only a predetermined amount of the steel is consumed and so that a large output may be obtained by the use of a relatively small quantity of equipment. This method is flexible and may easily be adapted to conform to the other treatments to which the steel is subjected.

The method which is adapted to accomplish the above results consists in general in merely dipping the steel sheets in the ferric sulfate etching bath of suitable concentration and at a suitable temperature, and then permitting the coating or film of ferric sulfate adhering to the surface of the steel to react thereon outside of the bath for a sufficient length of time to obtain the desired etch and at the same time to completely use the ferric sulfate thus adhering. According to prior methods, suitable acids such as sulfuric acid have been used for etching purposes, and in some instances ferric sulfate solutions have been employed. In every instance, however, the steel plates have been etched by immersing them in the bath, and holding them there until the desired etch is obtained. This is essential in the case of the sulfuric acid, as insufficient of the acid would remain on the steel to obtain the desired amount of etch, particularly since sulfuric acid is not as rapid as ferric sulfate in its etching power. Ferric sulfate solutions, on the other hand, are unsatisfactory, when the plates are held therein, as during the etching ferrous sulfate is formed and this not only markedly decreases the etching power of the ferric sulfate but renders it very difficult to determine how long to leave the plates in the rapidly deteriorating bath to obtain a uniform etch on each plate.

The effect of varying amounts of ferrous sulfate on the etching power of various ferric sul-

fate solutions is clearly shown by the following table, which represents the results obtained by making up 1000 grams of solution, in each case containing $FeSO_4$ and $Fe_2(SO_4)_3$ as shown, and immersing plates have an etchable surface of .876 sq. ft. at 66° C. for periods of time varying from two to five minutes and sufficient to obtain the average rates of etch per minute given:

Gm. $Fe_2(SO_4)_3$ per 1,000 gm. solution	Rate of etch in gm. Fe/sq. ft. etchable surface/min.		
	260 gm. $FeSO_4$/1,000 gm. soln.	180 gm. $FeSO_4$	70 gm. $FeSO_4$
220	.15	.97	2.40
200	.11	1.06	1.60
180	.11	1.11	1.42
160	.29	1.02	1.50
140	.68	1.08	1.42
120	.50	.91	1.09
100	.61	1.14	.97
80	.48	.74	.91
60	.34	.57	.68
40	.34	.49	.85

The sheets which are to be etched in accordance with the present invention may be unpickled sheets, sheets pickled with an inhibited acid or sheets pickled with uninhibited acid, such as sulfuric and muriatic acid. The use of sheets which have been previously pickled in an inhibited acid and are free from rust and scale is preferable; they may be etched either dry or wet, depending upon how soon after the pickling the sheets are etched. In carrying out the etching operation, the sheets are dipped in a strong ferric sulfate solution just long enough to give them a coating of the solution. The time required is usually the minimum time required by the handling apparatus to mechanically dip and remove the plates, which is usually a matter of 1 or 2 seconds. The sheets are then allowed to drain and the adhering ferric sulfate solution is allowed to react with the steel. The time required for this reaction depends on the temperature and strength of the ferric sulfate solution and upon the rate at which heat leaves the plate during the draining and reacting period. In general a period of two or three minutes is sufficient, but under certain conditions the time may vary anywhere from about ½ minute to about 10 minutes.

Elevated temperatures such as 70–100° C. are preferred for the ferric sulfate dipping bath. However, under certain conditions room temperatures may be used. For example, when only a light etch is desired, weaker solutions of ferric sulfate may be used, and such solutions, being less viscous than the stronger solutions, do not require raised temperatures for effective action. On the other hand, it is also possible to employ temperatures higher than 100° C., e. g. up to the boiling point of the solution, although such temperatures are less desirable for various reasons and usually not required. To maintain rapid reacting conditions the sheets are preferably protected from undue chilling or undue air currents leading to excessive evaporation of moisture from the adhering sulfate film.

Varying strengths of ferric sulfate may be successfully employed, depending upon 1) the amount of etch desired, 2) the temperature employed, and 3) the speed of reaction desired. Thus, solutions varying from about 10 to 45% of ferric sulfate are suitable, although in general it is preferable to use solutions varying from about 20 to 35%. If the ferric sulfate is too weak, insufficient ferric sulfate adheres to the steel surfaces to chemically react with enough iron in the steel to give the degree of etch necessary for good galvanizing. If the solution of ferric sulfate is much over 45% in strength the adhering film of ferric sulfate is so viscous that the reaction between ferric sulfate and steel is greatly cut down and is incomplete because of the immobility of the reacting, adhering film. A bath containing approximately 33% ferric sulfate, such as, a 35% solution of the commercial material known as "Ferrisul," gives good results.

At the end of the holding time, if properly calculated for the strength of solution used and temperature employed, all of the ferric sulfate has been reduced to the ferrous state by reaction with the steel surface, which means there is substantially no loss of active material. In sulfuric acid etching as usually practiced the sheets, even after washing, have a low pH, such as 1–2, whereas the hydrogen ion concentration or acidity of the steel surface after reaction with ferric sulfate is nearly neutral, being around 7. The sheet surfaces may be tested for the completeness of the conversion of the ferric to ferrous iron by adsorbing some of the liquid from the surface of the plate on a filter paper and analyzing for ferric iron.

The etched sheets are then washed free of adhering ferrous salts in a suitable washing machine such as those used in regular pickling operations, wherein the sheets are scrubbed with brushes, flushed with water streams and dried. After washing, the sheets may be returned for another dip in ferric sulfate or carried on to further operations such as galvanizing. The number of dips in 35% "Ferrisul" solution depends upon the type of steel being used and upon the method of galvanizing employed as well as on the type of galvanized sheet which is being produced. I have found that one dip in the 35% "Ferrisul" solution is equivalent to the removal by etching of about .9 gram of iron per square foot of surface.

This invention is essentially the process of dipping steel articles into preferably strong and relatively viscous ferric sulfate solutions preferably at elevated temperatures, thereby covering them with a thin film of the reactive ferric solution, and then allowing this film to react with and etch the steel surfaces by providing a short holding or reacting period. The etched articles are then washed and are ready for a second and similar treatment or for further operations such as galvanizing, tinning, etc. By the use of this invention it is possible in galvanizing mills to use an inhibited pickle for scale removal with its obvious advantages and at the same time obtain a steel surface which has been etched in a satisfactory manner so that the zinc coatings put on in the galvanizing pot are of a superior character. Moreover, this invention not only makes available practically 100% of the inherent etching power of the solution used, but substantially avoids contamination of the bath and the resulting slowing down of the etching operation.

As an example of this invention steel plates of No. 28 gauge, which have been previously pickled in inhibited sulfuric acid by the usual procedure, are immersed in a 33% ferric sulfate solution (35% "Ferrisul") at 80–90° C. for less than 5 seconds, removed and stacked either vertically or horizontally for at least 2 minutes. The

sheets are then washed with water and scrubbed with rotating brushes after which they may be dried. For the purpose of obtaining a tight coat the sheets are put through a similar and second cycle after which they may be stored either dry or wet until they are run through the regular fluxing and galvanizing operations.

De-zincing of samples of the sheets by immersion in a mixture of strong hydrochloric acid and antimony chloride showed that the zinc coating was in every way equal to that obtained on the same type of steel sheet which had been etched by the usual uninhibited sulfuric acid treatment, including the size and shape of the "spangle."

In the practice of this invention the process may be carried out in any suitable apparatus. For example, the sheets may be passed through a mechanism similar to that commonly used for the muriatic acid dip employed just prior to galvanizing where the steel sheets are continuously fed into a small tank containing the reacting solution. The sheets may then pass over suitable chain belts to allow for the holding or reacting period followed by a pass through a washing and scrubbing machine of the usual mill design. Where second and in rare cases third cycles are desired they are duplications of the first. It is obvious that by the use of this process steel articles and steel sheets in particular can be handled either on a continuous basis or by batches.

This invention is not limited to ferric sulfate since a similar process using ferric chloride gives good results. Ferric chloride, however, due to its lower viscosity, must be used in solutions of greater concentration than those of ferric sulfate in order to get an equivalent amount of retention on the sheet and hence an equivalent degree of etch. However, this is to some extent an advantage, as it is possible to use higher concentrations of ferric chloride solutions than is practical in the case of ferric sulfate without the material becoming too viscous. Thus, these higher concentrations render it possible to obtain an even higher degree of etch than is possible with ferric sulfate solutions. In some instances, solutions of as high as 50% ferric chloride are suitable.

It is not essential that the ferric sulfate or chloride be applied by dipping the sheets in a ferric sulfate or chloride solution and then withdrawing them, since the solution may be sprayed on or applied in any other manner which will form a relatively uniform film of the solution on the sheets.

This invention is particularly useful in galvanizing steel sheets, but it can also be advantageously employed in preparing iron sheets for other coatings such as electroplating, enameling, painting or other protective or ornamental surfacing, such as tin or terne coatings.

This application is a continuation-in-part of my pending application Serial No. 148,589, filed June 16, 1937.

What I claim is:

1. In the manufacture of galvanized steel objects the method of preparing the objects for galvanizing which comprises pickling them in an aqueous acid solution containing an inhibitor and then etching them by applying a relatively uniform film of an aqueous ferric sulfate solution and permitting the film to react with the steel, removing the reaction products and then galvanizing the article.

2. The method of galvanizing iron objects wherein an inhibited acid is used to pickle them whereby a tenaciously adhering coat having "spangle" characteristics equal to those obtained when an uninhibited acid is used is obtained comprising applying a relatively uniform aqueous film containing a substance selected from the group consisting of ferric sulfate and ferric chloride to the previously pickled object and permitting the film to react with the iron, removing the reaction products and then galvanizing.

3. The method of treating iron objects which comprises pickling them in an aqueous acid solution containing an inhibitor, dipping the object into an aqueous solution of ferric sulfate, immediately withdrawing it and permitting the layer of ferric sulfate on the surface thereof to react with the iron, removing the reaction products, and then galvanizing the iron object.

4. The method of treating iron or steel objects prior to applying a coating thereon which comprises dipping the object into an aqueous solution containing from about 10 to 45% of ferric sulfate and maintained at a temperature of about 25 to 125° C., immediately withdrawing said object, whereby a film is formed thereon, permitting the resulting film of ferric sulfate solution on the surface of said object to react on said surface for about one-half to ten minutes, and thereafter washing said surface to remove the residual solution and reaction products.

5. The method of treating iron or steel objects prior to applying a coating thereon which comprises dipping the object into an aqueous solution containing from about 10 to 45% of a substance selected from the group consisting of ferric sulfate and ferric chloride, and maintained at a temperature of about 25 to 125° C., immediately withdrawing said object from the solution, permitting the resulting film of ferric salt solution on the surface of said object to react on said surface for about one-half to ten minutes, and thereafter washing said surface to remove the residual solution and reaction products.

6. The method of treating iron or steel objects prior to applying a coating thereon which comprises dipping the object into an aqueous solution containing from about 20 to 35% of ferric sulfate, and maintained at a temperature of about 70 to 100° C., immediately withdrawing said object, whereby a film is formed thereon, permitting the resulting film of ferric sulfate solution on the surface of said object to react on said surface for about 2 to 4 minutes, and thereafter washing said surface to remove the residual solution and reaction products.

7. In the manufacture of galvanized steel objects the method of preparing the objects for galvanizing which comprises pickling them in an aqueous acid solution and then etching them by applying a relatively uniform aqueous film containing a substance selected from the group consisting of ferric sulfate and ferric chloride, permitting the film to react with the steel, removing the reaction products and then galvanizing the article.

8. The method of treating iron or steel articles which comprises applying a relatively uniform aqueous film containing from about 10 to 45% of a substance selected from the group consisting of ferric sulfate and ferric chloride, permitting the adhering film to remain on the metal surface until the ferric ions of said substance are substantially entirely converted to ferrous ions, and then removing the reaction products.

9. The method of treating iron or steel articles

which comprises applying a relatively uniform aqueous film containing about 10 to 50% of ferric chloride, permitting the adhering film to remain on the metal surface until the ferric ions of said chloride are substantially entirely converted to ferrous ions, and then removing the reaction products.

10. The method of treating iron or steel objects which comprises dipping such an object into an aqueous ferric chloride solution containing about 10 to 50% of ferric chloride, immediately withdrawing said object, whereby a film is formed thereon, permitting the adhering film to remain on the metal surface until the ferric ions of said chloride are substantially entirely converted to ferrous ions, and then removing the reaction products.

11. The method of treating iron objects prior to galvanizing them which comprises dipping the object into an aqueous solution containing about 10 to 45% of ferric sulfate, immediately withdrawing said object whereby a film is formed thereon, and permitting the film of ferric sulfate adhering to the iron to remain thereon under reacting conditions for from one-half to ten minutes and then removing the reaction products.

12. The method of treating iron objects which comprises pickling them in an aqueous acid solution containing an inhibitor, dipping the object into an aqueous solution of ferric chloride, immediately withdrawing it and permitting the layer of ferric chloride on the surface thereof to react with the iron, removing the reaction products, and then galvanizing the iron object.

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