

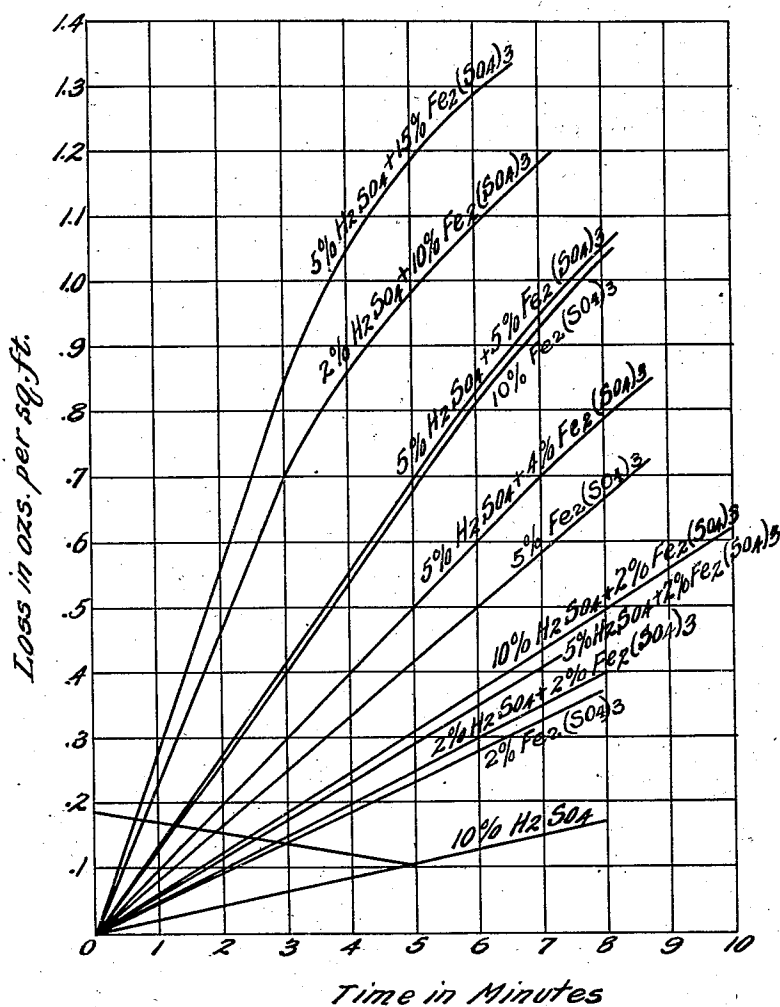
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RESURFACING OF METALS

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RESURFACING OF METALS

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This invention relates to the resurfacing of metals, particularly low carbon ferrous metals, to render such metals amenable to subsequent finishing treatment such as metal coating, fused oxide coating and the like.

As is known a tremendous tonnage of ferrous metal, in the form of sheets and formed articles are coated for the purpose of preventing corrosion of the ferrous base. Thus the ferrous sheets and formed articles are provided with a coating of zinc metal, as in galvanizing; with copper, nickel, chromium and the like as in electroplating, with aluminum as in calorizing and the like. In order to insure the desired adherence of such surfacing it is essential that the ferrous basis metal be free from foreign materials, and particularly from iron oxides. In the past therefore a necessary preliminary to the application of protective coatings, has been a thorough pickling of the basis metal.

In the past many different types of pickling baths have been suggested. Up to the present time the most effective and economical pickle for the treatment of low carbon ferrous metals consists essentially of a sulphuric acid solution. As will be seen more fully hereinafter this pickle presents many disadvantages such as a relatively slow chemical attack on the oxides, a relatively rapid depletion of the bath and a high economic loss in discarded solutions.

The present invention relates to an improved method of pickling; in one aspect the invention comprehends the production of a novel type of pickling solution; in another aspect the invention comprehends a method of improving and/or regenerating old pickles. As will be seen more fully, because of the peculiar efficacy and accelerated action of the novel pickle, improved methods of fabrication of steel sheets and formed articles are made possible, particularly, and didactically, the continuous production of corrosion resistant steel sheets, such as galvanized steel sheets.

In the typical method of production of steel sheets by the hand mill method, the steel is rolled to a certain width, gauge and the desired or specification length. In the continuous method the steel is rolled to the desired width and gauge and to a length of several hundred feet. In the latter method the strip is coiled and shipped as such, or sheets may be cut from the coil to the individual lengths that may be ordered. During the process of fabricating sheets or coils under either of the above methods, iron oxides tend to form on the surface. These ox-

ides are of different types or characteristics depending upon the particular treatment the steel has undergone and result from the rolling operations, from the action of gases which permeate into the annealing box, from gas positively introduced into the annealing box during the annealing operation, from spontaneous air oxidation when the material is removed from the annealing process and from subsequent atmospheric oxidation. The type of characteristics of such oxides vary according to the temperature of formation, the composition of the gas in contact with the steel base and the special physical characteristic of the steel base itself. When the metal is subjected to the combined effects of an oxidizing atmosphere and high temperature, the resulting scale is usually very heavy consisting of a mixture of ferrous oxide, ferric oxide, and ferrous-ferric oxide. It is generally agreed that in pickling this type of scale with a solution of sulphuric or hydrochloric acid certain of these oxides are attacked by the acid and are removed and that, because of perforations in the oxide coating the pickle contacts with the subjacent metal which latter displaces the hydrogen of the acid and this evolved hydrogen loosens and pries off the oxide layer. This latter action is utilized to an accentuated degree in electrolytic pickling.

As the reaction of the acid on the oxide layer progresses the pickling solution tends to become saturated with the reaction products, namely ferrous sulphate or ferrous chloride. As the quantity of the ferrous salt increases the pickling action tends to be retarded or inhibited so that in time it is necessary to discard the solution and utilize a fresh pickle. The solution which is thus discarded however contains much free acid which has a real value. In some circumstances this acid content is in fact sufficiently large to be effective for pickling were it not for the presence of the ferrous salt. For example, when the ferrous sulphate in a pickling solution of this character amounts to about thirty per cent. at a temperature of 200° F., the bath is reduced in efficiency for any additional sulphate which is formed is precipitated. When this fact is combined with the fact that additions of acid over 15 per cent do not improve the pickling action it is apparent that, in the very nature of these older pickles, a large quantity of the valuable acid was lost in the discarded solutions.

In some plants the depleted solution is dumped into the sewerage system while in other plants

attempts are made to reclaim the acid content or the iron content. For example, in certain plants the acid is neutralized with scrap iron. It has also been proposed to treat these expended pickle solutions so as to convert the ferrous sulphate into valuable products such, for example, as ferric sulphate available for coagulants and the like.

In the typical practice the solution is dumped periodically when the bath has attained a high, although not necessarily saturated, solution of ferrous sulphate. A fresh solution is made up to replace that discarded. This prior practice was quite expensive in that large amounts of acid were lost in the discarded solutions, or when attempts were made to recover such acid considerable expense was involved in the regeneration.

It has now been found that the efficiency of acid pickles may greatly be enhanced and the effective period of use of a given acid pickle considerably prolonged by utilizing certain agents in the pickle solutions; specifically it has been found that the utilization of an aqueous solution containing available ferric ions, and also the addition of ferric ions to a pickling solution such as a sulphuric acid bath markedly increases the pickling efficiency of new solutions and, unexpectedly, maintains a higher efficiency of the pickle even when such pickle is substantially saturated with ferrous compounds.

As will be seen more fully, the rate of pickling is, in general, proportional to the concentration of the ferric ions, alone, or in combination with mineral acids, in the bath so that the present invention presents a simple and effective method for controlling the speed or rate of pickling and substantially independently of the acid concentration.

The unexpected results derived from the utilization of the invention, and its potentialities in the art, particularly in continuous pickling, will be more readily appreciated from a consideration of actual comparative tests of typical sulphuric acid pickles on the one hand, aqueous solutions of ferrous salts, and aqueous solutions containing both ferric salts and mineral acids, such as sulphuric, on the other, that is to say, sulphuric acid pickles containing predetermined percentages of ferric ions.

In one series of tests, pieces of strip steel, of the same area, and cut from the same stock, were immersed in a typical partially expended pickle, and similar specimens were treated in this same pickle to which was added a ferric salt, specifically ferric sulphate. The typical or control solution contained 3.1% of sulphuric acid and 18.7% of ferrous sulphate. Immersion of a steel sample in this bath for a predetermined time and temperature showed a loss in weight of 0.067 ounce per square foot. The improved solution analyzed 3.1% sulphuric acid, 18.7% of ferrous sulphate and 5% of ferric sulphate, that is, it was identical with the control solution except for the addition of the ferric salt. Immersion tests of the same type of steel specimen at the same temperature and for the same period of time showed a loss in weight of 0.43 ounce per square foot. Such tests show, therefore, that the addition of moderate amounts of a ferric salt increases the activity of the bath to a surprising degree. Preliminary investigation also conclusively proved that the activity of hydrochloric acid pickles could be greatly accentuated by the addition of ferric ions, although not to the same quantitative extent as the sulphuric acid baths.

In order more clearly to explain the principles

of the invention there is shown in the accompanying drawings a graph in which the loss in weight of the specimens are plotted against time for a series of simple ferric ion-containing solutions and for sulphuric acid baths having varying ferric ion concentrations. In this graph a straight 10% sulphuric acid bath serves at the one time as a control and as illustrative of prior practice.

A striking feature which is clearly illustrated in the graph is that the predominating factor in accelerating the action of the bath is the percentage of the ferric ions and that, correlatively, the time of cleaning is substantially inversely proportional to the ferric ion content. Thus the bath which contains 2% of sulphuric acid and 2% of ferric sulphate is substantially twice as active as a bath composed of 10% of sulphuric acid. Also it will be seen that a simple aqueous solution of 2% ferric sulphate is quantitatively substantially twice as active as the 10% sulphuric solution. Similarly it will be observed that when 2% of ferric sulphate is added to the 10% pickle solution the activity is very markedly increased. In other words, addition of ferric ions greatly accelerates the activity of the bath over a very broad range of acid concentrations.

The striking effect of the addition of ferric ions to a bath which is low in acid, as will be appreciated by those skilled in the art, establishes the possibility of prolonging the activity of the typical or older acid pickles. Thus baths which, under the old practice, has to be discarded because of the inhibiting effect of ferrous sulphate, but which nevertheless did contain appreciable amounts of acid, may, under the invention, be continued in use or regenerated by insuring the presence of a predetermined percentage of ferric ions. Another salient feature which is illustrated by the result shown in the graph, is that the cleaning or pickling time is substantially inversely proportional to the ferric ion concentration. This is particularly fortuitous in that it insures a more accurate control of pickling and establishes a wide potential flexibility in operations. Thus by adjustments of the ferric ion concentration a particular bath can quickly be modified to treat different types of stock or to vary the degree of cleaning within fixed time periods.

In order more clearly to explain the operation of the invention the utilization of the improved type of bath will be described with particular reference to galvanizing operations. It will be understood, however, that this is merely explanatory and that the improvements described herein may be utilized in any analogous circumstances, that is to say, where ferrous metal is to be pickled to remove loose and adherent oxides or otherwise to prepare the surface for subsequent operations.

As is known, in galvanizing, the speed of output is practically established by the gauge of the sheet being galvanized since for the thicker sheets more time is required to allow the sheet to attain the temperature of the zinc bath and to form a strain free alloy. Also, when highly adherent zinc coatings are desired which will withstand severe cold working, the speed of travel through the bath is slower than for a commercial coating, such as for roofing purposes, where the material does not have to withstand severe cold working stresses but must have a substantial coating of zinc. The economies in the galvaniz-

ing operation, therefore, depends very largely upon the speed of travel through the system.

In producing galvanized stock also adjustments of the pickling operations are necessary to secure efficient results from different types of starting material. Thus sheet stock produced by a hand mill or continuous type of mill has a relatively adherent oxide coating. To obtain a commercial zinc coating on this material it is necessary only to remove this oxide layer. However in order to produce what is known as a tight coat it is the customary practice to give the stock a prolonged pickle to insure thorough cleaning and improve the bond between the zinc and subjacent metal. In the usual practice when stock was to be prepared for the application of a "tight coat" the existent bath, even though only partially used, was generally discarded and a fresh bath was made up. By utilizing the principles of the present invention such partially depleted baths can be regenerated by addition of a suitable ferric salt and employed with excellent results.

Again, the recently developed method of producing relatively thin sheets in a continuous cold strip mill does introduce some special problems in the pickling stage. This type of stock has a very smooth surface and apparently has a very thin film of oxide, formed as a result of annealing operations or of atmospheric oxidation. Such oxide, being formed on a smooth or polished surface is of a special texture and is very difficult to remove by the usual pickling solutions due probably to the fact that it does not present the foci or interfaces for reaction with the acid to as great a degree as other types of oxide coats, or rougher surfaces. In the pickling of this stock the attack by the bath is quite uneven and some parts of the steel base are cleaned long before other sections. This characteristic is especially disadvantageous when this material is attempted to be used in continuous pickling where the time element is of peculiar importance. Baths produced according to the present invention are particularly effective on this type of stock because of the accelerated as well as uniform action of the bath.

Another interesting and valuable characteristic of the improved baths is their specific action on more or less scarified stock. As is known, when the surface of a steel sheet contains depressions or pits such as the so called "seams" and "scabs," the oxide films over these depressions are not attacked by the ordinary acid solutions until the flat areas of the sheet have been cleaned. With pickles containing active ferric ions, however there appears to be a preferential action on the oxides over these depressions. In pickling this type of stock therefore the ferric ion-containing pickles have a greatly accelerated specific action as compared to older types of baths.

The baths described herein possess special merit in batch pickling. In the customary batch pickling now employed in the art from about twenty-five to about one hundred sheets of appropriate thickness are simultaneously immersed in the solution and a certain time cycle is allowed for the pickling. Where thorough or drastic pickling is desired this time cycle is lengthened. In the actual mechanism of the pickling action a certain time is necessary to allow the solution to wet the surface of the sheet and thereafter it functions selectively, so that the pickling time is established by the period required to clean the most resistant portion. The

ideal conditions for pickling therefore is the utilization of a pickle of accelerated and preferably adjustable activity such that the pickle baths can be aligned with the galvanizing bath and synchronized with the maximum thruput or speed of the galvanizing stage. These criteria are admirably fulfilled when employing the ferric ion-containing baths, for as indicated in the graph, the speed of cleaning can be controlled over wide ranges by the simple expedient of adjustment of the ferric ion concentration. In other words the ferric ion concentration, being rapidly adjustable can be correlated with the optimum operations of the galvanizing baths and the efficiency of a given pickling bath maintained over periods greatly prolonged as compared to older types of baths.

In this and other types of operations, as will be appreciated the pickling efficiency of a bath can be maintained by continuously or intermittently drawing off a modicum of the solution and correspondingly replenishing with a ferric salt, alone, or if desired, together with a moderate amount of acid.

While, as noted above baths produced under the present invention possess special merit in batch pickling, for accelerating pickling action and minimizing acid effluent, they present striking efficacy for continuous pickling as associated for example with the recently developed method of continuous sheet production. In the old process the time of travel of a sheet through the galvanizing pot was between substantially fifty to ninety feet per minute. At the present time the pickling baths associated with continuous sheet production are about sixty feet long and are placed four in sequence. As compared to earlier pickling solutions the novel pickles described herein are so accelerated in their cleaning action that continuous galvanizing is made possible, for example, one tank of substantially eighty feet in length is sufficient to provide for normal galvanizing operations. Where space permits maximum thruput through the galvanizing stage can be insured by utilizing two pickling tanks each substantially fifty feet in length.

The peculiar specificity of action of the ferric ion-containing solution in producing an accelerated action on strips which contain depressions or pits and where a differential potential could exist presents the possibility of further speeding up the process. Thus advantage can be taken of this accelerated action by utilizing an arrangement of scratch brushes at the fore part of the pickling bath. Such brushes may be made of any suitable alloy, such as an 18-Cr-8Ni-3Mo stainless steel, which is resistant to the pickle solution. In this manner, that is to say by fully utilizing the accelerating action of the ferric ion-containing solution it is thus possible to satisfy the maximum requirements of the continuous galvanizing stage with a single pickling tank sixty feet long, or thereabout.

In the preferred installation for continuous pickling means should be provided to minimize the drag out losses of the pickle. For this purpose a series of doctor blades or similar wiping arrangement may conveniently be placed adjacent the exit of the pickling stage. This may be supplemented with or substituted by a water scrubbing the liquid from which could be used in the bath or for make up solutions.

As will have been appreciated the specific bath mixtures which are to be employed will depend upon the circumstances of a particular opera-

tion such as, the thruput speed, the degree of pickling desired, and the like. In the nature of the improved solutions the most economical mixtures are those low in ferric sulphate. The efficiency of the bath can be maintained by periodic analysis for from one to eight hour periods and the corresponding adjustment of the ferric ion concentration by the addition of replenishing salts or solutions containing available or potentially available ferric ions. In continuous pickling the efficiency of the bath may be maintained by continuously admitting an adjustable stream of ferric ion containing replenishing agent in the form of a solid or solution. This admission may be so controlled as to maintain the ferric ion concentration at a substantially determined value or at a value which increases proportionally to the decrease in acid content.

It is also particularly to be observed that operating according to the present invention insures reclamation economies not attainable under earlier methods. In the reclamation of the iron content of spent pickles the optimum solution is one very low in free acid and substantially saturated with ferrous sulphate, because the acid requires the use of neutralizing agents such as lime or reactants such as scrap iron. Under the present invention operations can be efficiently conducted when utilizing a minimum acid content and the solution can be drawn off periodically at the saturation point of ferrous sulphate thereby minimizing storage areas, reclamation capacity and the quantity of neutralizers.

It will also be noted that the assurance of a very low acid content in the spent liquid is of special importance in those plants where such liquid is dumped into streams. The acid content of this effluent is probably the most harmful component. Ferrous sulphate has but small affinity for oxygen whereas ferric sulphate is a strong oxidizing agent either alone or in combination with acid. Furthermore trivalent salts like ferric sulphate and ferric chloride serve in themselves as effective coagulants for suspended matter.

It will be appreciated that while mention has been made of ferric sulphate as the addition agent this is given merely as a typical example of insuring the presence of available ferric ions in the pickle. The same results can be obtained by adding other suitable ferric salts to the bath such for example as ferric oxide in appropriate form.

As will be appreciated by those skilled in the art, the baths of the present invention may be operated at any temperature up to the boiling point of the solution. By modifying the temperature in conjunction with the ferric ion and the acid concentration a wide range of control of pickling action is available.

It will be understood that while pickling operations have been described in which the novel pickle solution alone is employed, such novel pickles may be used in association with other pickling methods. Thus, where desired, the improved type of pickling described herein may be used for batch or continuous pickling and may be followed by ordinary pickling with a typical sulphuric acid. For example where a customer has his equipment devised for pickling sheets made by the hand mill process, a preliminary pickling with a ferric ion-containing solution will provide a sheet or coil produced by cold rolling strip steel in such a state that the customer may use his equipment as usual in order to obtain the desired surface condition. Again, where circumstances so dictate, the stock may be given a preliminary pickle in the usual type of bath and then may be finished, either immediately or immediately, in the ferric ion-containing solution. These and other desirable associations of the improved pickling with other forms of cleaning or coating of ferrous surfaces are comprehended within the spirit of the invention.

While preferred modifications of the invention have been described it is to be understood that these are given to exemplify the underlying principles involved and not as limiting the invention to the particular processes or baths described for illustration.

I claim:

1. A method of pickling cold rolled strip steel which comprises contacting the surface of the steel for a predetermined time with an aqueous solution which contains substantially 5% of sulphuric acid and substantially 4% of ferric sulphate.
2. A method of pickling cold rolled strip steel which comprises subjecting the steel to the action of a solution containing available ferric ions and subsequently subjecting the so-treated steel to the action of a sulphuric acid pickle.

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