Feb. 9, 1943. W. E. MARSHALL 2,310,451

PROCESS OF COATING METAL ARTICLES WITH MOLTEN METAL AND OF PREPARING METAL ARTICLES FOR HOT COATING

Filed June 17, 1940 2 Sheets-Sheet 1

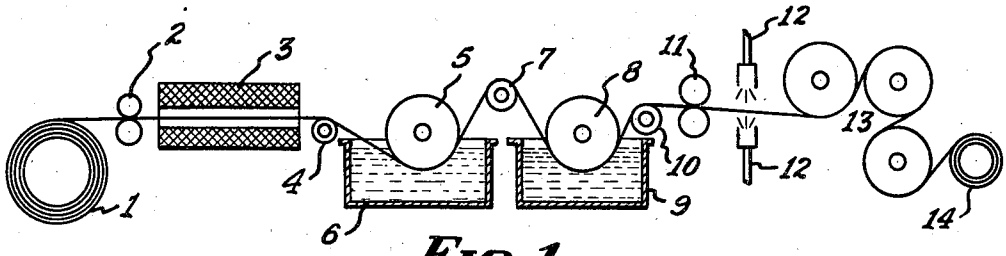



FIG. 1.

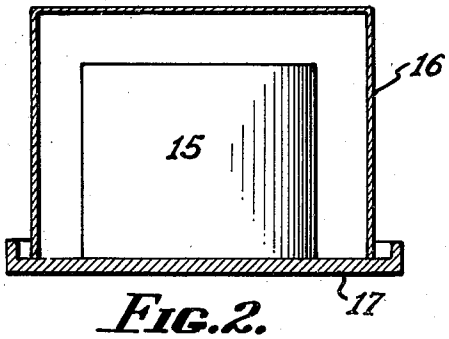



FIG. 2.

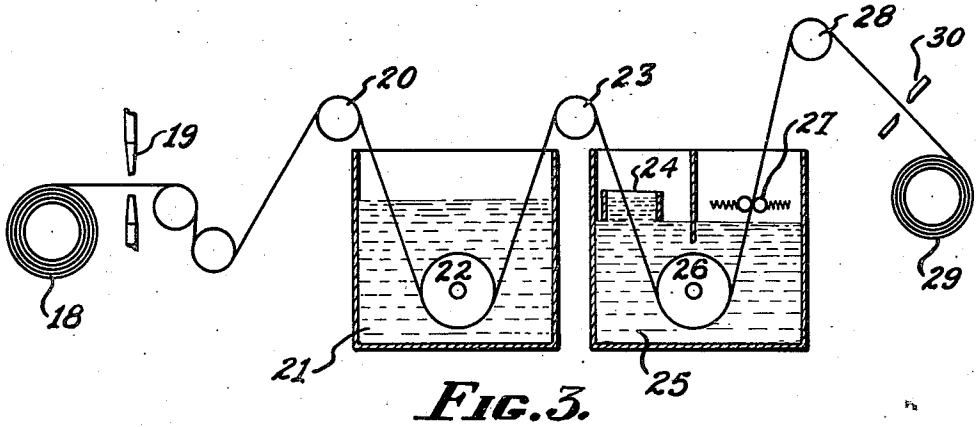



FIG. 3.

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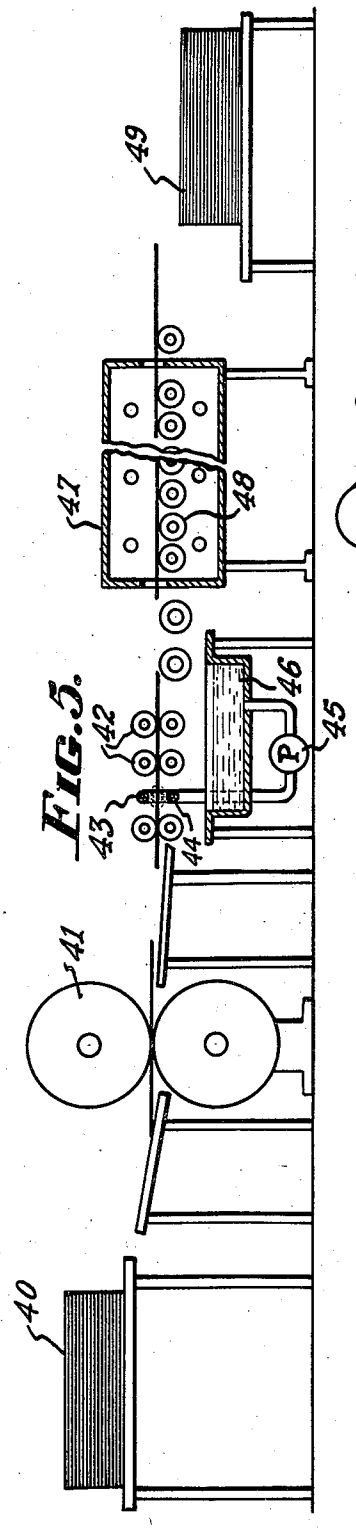



FIG. 5.

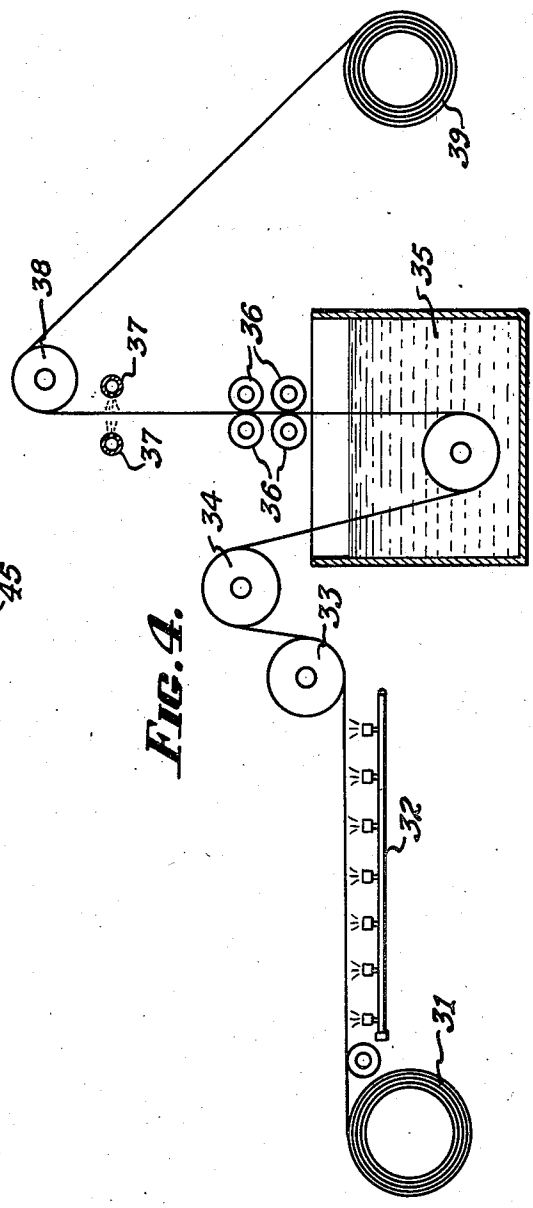



FIG. 4.

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# UNITED STATES PATENT OFFICE

2,310,451

## PROCESS OF COATING METAL ARTICLES WITH MOLTEN METAL AND OF PREPARING METAL ARTICLES FOR HOT COATING

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Application June 17, 1940, Serial No. 340,912

3 Claims. (Cl. 148—7)

My invention relates to the coating of metal articles with a dissimilar molten metal by hot dipping, and in particular to the galvanizing of ferrous metals, in connection with which it will be described in an exemplary embodiment. It has been known that phosphorus in iron or steel increases the adherence of zinc and other coating metals to the base metal. The alloying of phosphorus with iron or mild steel is not only a matter of some expense, but has the effect of making the base metal harder, less ductile and more resistant to the passage of electric current. It has been suggested that iron or mild steel articles be given a treatment whereby phosphorus became alloyed with the base metal only at the surface thereof, whereby to avoid the disadvantages mentioned above. Hitherto, however, there has not been available a commercially satisfactory treatment for this purpose, or one which did not involve expensive equipment, elaborate control means, and considerable danger to the workmen in charge of the process.

Objects of my invention are the provision of means and a method for imparting phosphorus to external layers only of metal articles, which means are inexpensive in first cost and in operation, which do not require any element of human control to achieve a uniform and satisfactory result, and which process is positive and uniform in action as well as inexpensive in materials required, and does not constitute in any wise a health hazard.

More specifically, objects of my invention are the provision of means and a process which may be depended upon in substantially automatic operation to produce a uniform addition of phosphorus to the surfaces of metal articles, which will satisfactorily prepare the surfaces of metal articles for coating if these surfaces are initially scale free, but substantially irrespective otherwise of their surface condition, and an improved general method of hot coating metal articles whereby improved results are secured at insignificant added expense.

These and other objects of my invention, which will be set forth hereinafter or will be apparent to one skilled in the art upon reading the specification, I accomplish by that method and apparatus of which I shall now describe certain exemplary embodiments.

Reference is made to the drawings accompanying this specification wherein:

Figure 1 is a diagrammatic elevational view of a preferred apparatus for preparing metal for annealing.

Fig. 2 is a diagrammatic representation of an annealing stage.

Fig. 3 is a diagrammatic representation of a galvanizing stage.

Fig. 4 is a diagrammatic representation of an alternative means and procedure of preparing the metal for annealing.

Fig. 5 is a similar representation of an apparatus and method effective with individual sheets.

My process is applicable to metal articles in any of their forms, and including but without limitation sheets, strip and wire.

My process involves broadly aspects of cleaning, applying a phosphorus bearing substance, annealing, and coating, with usually certain intermediate steps as will hereinafter be set forth; but I have in my method a new coaction and interaction of the several steps as well as specific novelty of certain of the steps themselves. This will become apparent upon describing the preferred form of the process as set forth in Figs. 1, 2 and 3.

In Fig. 1, 1 represents a coil of strip or wire in scale free condition. If the metal has been reduced by hot rolling its surfaces will have been freed of the hot mill scale by pickling. Or the metal may be green, or annealed, cold rolled strip, which may or may not have oil on its surfaces. The metal is withdrawn from the coil by pinch rolls 2 or some other feeding device, and is set through a furnace 3, in which the atmosphere is kept oxidizing preferably by being open to the air. This furnace may be electric, gas or oil fired. When gas or oil is used a muffle is usually installed, but is not in all cases necessary depending upon the type of burner and the furnace design. In the furnace 3, oil or hydrocarbon material on the surface of the metal is volatilized or burned up, and a thin coating of oxides of controlled character is produced on the surface of the strip. The oxide may vary in thickness from an amount invisible to the eye to an amount which will vary in color from a light straw to blue or even to gray, but should preferably not be thicker, since thin oxides can be more quickly removed by the subsequent operations.

The strip or wire then passes over a supporting roll 4 and into a water tank 6 for preliminary cooling, in which tank it is held down by a roll 5. The water tank is not in all instances necessary; but is usually an operative convenience. It precools the strip or wire to the extent of preventing overheating of the bath to follow, and depending upon the speed of travel of the

wire or strip, leaves enough heat in it to make for rapid drying after it has passed through the acid bath.

The material next passes over roll or sheave 7 and under roll 8 so as to pass through a tank 9. This tank contains a solution of phosphorus bearing compound, preferably one of the phosphoric acids in water solution. As the strip or wire passes out of the bath 9 over the roll or sheave 10 its surfaces are uniformly coated with the acid solution. Pinch rolls 11 are for the purpose of regulating the amount of solution left on the surface. Usually there is enough heat in the wire or strip to make for rapid drying of its surfaces. Where however this is not the case, the material may be rapidly dried by means of burners 12. The dried material is coiled on a coiler 14. I prefer to provide a tensioning means 13 to make possible tight and even coiling.

Figure 2 is a diagrammatic representation of an annealing stage in which the coil 15 is annealed in a box 16 on the base 17 with the usual sand or other seal and in a controlled atmosphere.

In Fig. 3 the remaining steps of an exemplary galvanizing procedure are shown diagrammatically. The coil 15, having been annealed is decoiled at 18. Welding means 19 may be provided to join together the ends of coils whereby to make the galvanizing continuous. A looping means is usually provided in connection with the welder. The wire or strip passes over roll 20 into a tank 21 of hydrochloric acid solution, in which it is held down by a roll 22. Thence it passes over roll 23 and through a flux box 24 into the galvanizing pot 25. A guide roll 26 or equivalent is included in the galvanizing pot. The wire or strip may be withdrawn through exit rolls 27 if desired, and carried over roll 28 to a coiler 29. Shearing means are indicated at 30.

I now take up the relationship of the treatments in the exemplary procedure which has now been outlined. In the oxidizing furnace 3 the material has its surfaces freed from greasy or oily substances which would prevent those surfaces being uniformly and completely wet by the phosphorus bearing solution. Ordinarily I employ temperatures in the furnace such that the strip reaches a temperature between 500° F. and 700° F.; but these temperatures are not limiting, since time is also a factor. Longer times at lower temperatures and shorter times at higher temperatures are available. The production of oxide coating is a consequence of the treatment; but is advantageous if thin and controlled as will hereinafter be set forth.

The water cooling of the sheet or strip makes it possible to keep the acid solution relatively cool. This has the advantages referred to above, and additionally prevents an excessive amount of pickling in the acid solution, resulting in economy since less phosphoric acid is converted into iron phosphate.

A certain amount of pickling occurs in the acid tank 9, especially of the thin oxide film produced in the furnace 3. This is advantageous in that it helps to clean the surface and produce a more uniform wetting and adherence. Too much pickling, with consequent formation of iron phosphate, is not to be desired.

The primary purpose of the treatment in tank 9 is to coat the strip or wire uniformly with the phosphorus bearing substance. Instead of phosphoric acid I may use any soluble phosphorus-bearing salt. Where a salt is used which in solution has no pickling action on the strip or wire, for example, sodium phosphate, it may be found desirable to impart a pickling action to the bath by adding hydrochloric acid to it, for example.

The strength of the phosphoric acid solution used in the tank 9 is not critical. Ordinarily I employ a solution of 20 to 30% by weight. The amount of phosphoric acid left upon the strip is determined by the surface texture of the pinch rolls 11 as well as by the concentration of the solution. The surfaces of the rolls can be made of rubber, cloth or other materials. The purpose is to secure on the surfaces of the strip or wire a uniform coating of such a weight of phosphorus bearing substance as will give the desired amount of phosphorus per unit area upon dissociation. For obtaining good galvanizing coatings amounts of imposed phosphorus bearing substance equivalent to 0.01 to 0.03 gram of phosphorus per square foot of surface of the metal being treated are sufficient. The effect of larger amounts of phosphorus up to 0.06 gram per square foot and beyond is a consistent though slower improvement. Sometimes difficulties with galvanizing operations begin to be experienced at around 0.10 gram per square foot. It is somewhat difficult to obtain uniform coatings of the phosphorus bearing substance on the metal surfaces where the larger amounts are employed. For excellent results, however, it is not necessary to go to the higher quantities. Based upon equivalent phosphorus contents, it will be within the skill of the worker in the art in the light of these teachings to control the strength of his solution to give the desired result.

The annealing indicated in Fig. 2, of course, softens the strip or wire, and especially where the final product is to be subjected to drawing or bending, is desirable for this purpose. Where an anneal before galvanizing is desirable from the standpoint of the ultimate qualities of the product, the anneal at the stage given is substituted for any other final anneal which would be employed, and to this extent does not increase the cost of the product.

But the anneal has a special function in connection with my process for producing a surface alloying with phosphorus, in that it is during the anneal that the phosphorus is freed by reduction of the phosphorus bearing substance, and is caused to enter the surface of the base metal. The anneal must be carried on in the presence of a reducing gas, but any available reducing gas will serve, including but without limitation, hydrogen, D. X. gas, dissociated ammonia, cracked butane and the like. During the anneal the phosphorus bearing substance on the strip or wire (including such iron phosphate as may be present) is reduced, and the phosphorus enters into an alloying relationship with and is absorbed by the metal surfaces. Also any traces of oxide remaining upon the metal surfaces are reduced.

The temperature and time of annealing should be controlled to get the proper reduction and alloying of the phosphorus with the surface of the metal. The higher the temperature the shorter the annealing time required. At usual box annealing temperatures, ranging from 1000 to 1400° F., the time required for heating and cooling is sufficient. At much higher temperatures such as 1800° F. or above the time required is decreased to around two or three minutes so that the process can be carried on as a continuous strip anneal.

The addition of phosphorus to the surface of the base metal is thus accomplished without danger to the workmen and without the production of dangerous fumes to any degree which merits practical consideration.

The mode of application of a phosphorus bearing substance and the dissociation of the substance in the manner described is preferred by me as giving a coating which is not only effective but is uniform. The addition of phosphorus to the surface of the metal may be accomplished without precoating by including in an annealing box or furnace a container of phosphorus bearing substance such as phosphoric acid, where the material being treated is bright and clean and where the atmosphere is maintained in a reducing condition. Where the fumes can get at all parts of the surfaces of the metal, this procedure is effective; but difficulty is experienced frequently with unequal additions of phosphorus especially in connection with coiled strip.

While I have diagrammatically indicated a box annealing for the purposes herein set forth, I am not restricted to this but may employ a continuous annealing in a furnace in which a suitable atmosphere can be maintained. Also I may conduct the material direct from a continuous annealing furnace to the pot of molten metal while protecting it by means of an inert or reducing atmosphere, thus eliminating the necessity of a subsequent acid treatment, and the use of a flux in some instances. For many uses, however, a box annealing is desired to impart desirable physical properties to the material. Where the material is annealed in coil or sheet form there will usually occur a period of exposure to the open air after the annealing and phosphorus adding treatment, which exposure may vary from a few minutes to a prolonged storage period. Where the material has thus been treated, I prefer to pass it first through a tank 21 containing hydrochloric acid solution before passing it through the flux into the galvanizing coating or metal support.

The use of a furnace as such for the oxidizing step is not in all instances necessary. In Fig. 4 I have shown the material being uncoiled at 31 and passed over a series of gas burners 32 to burn hydrocarbon substances from its surface. It may next be passed over rolls 33 and 34 directly into a tank 35 of phosphoric acid solution, thus illustrating the omission of the cooling means and step illustrated in Fig. 1. For control of the amount of the solution remaining on the strip or wire, I may employ a series of rolls 36 illustrated in Fig. 4 whose surfaces may be composed of rubber, cloth or other material. Drying instead of being accomplished by burners may be accomplished by air blasts from means 37. Material so treated may be passed over roll 38 and coiled as at 39 preparatory to annealing in any of the ways set forth above.

In handling materials the surfaces of which have recently been pickled, the oxidation step may be in instances omitted and satisfactory results still obtained. In Fig. 5 a stack of pickled sheets 40 is shown on a table preparatory to being passed through temper rolls 41. The sheets are then individually carried by conveyor means 42 past a stage at which the phosphoric acid solution is sprayed on their surfaces by means 43 and 44. The spray means is connected through a pump 45 to a tank or reserovir 46 of the solution, which tank is also preferably placed so as to catch the overflow from the sheets. One or more pairs of the rolls 42 may also assist in controlling the amount of solution remaining on the sheets. Drying of the coated sheets may, if desired, be accomplished in an oven or furnace 47, from which the sheets are carried on conveying means 48. After delivery from the oven, the sheets may be stacked preparatory to annealing as at 49.

As an example of my phosphorizing process I have illustrated the case in which it is applied after the material has been cold reduced to its finished gauge. This is not necessary, however, as the treatment can be applied at a gauge intermediate in the cold reduction or following the hot reduction and preceding any of the cold reduction.

In order to obtain certain physical properties of the base metal it may be in certain cases desirable to follow my phosphorizing treatment by one or more subsequent anneals. I have found that this can be done without damage to the phosphorized surface if a non-oxidizing atmosphere is maintained during the said subsequent anneals.

Modifications may be made in my invention without departing from the spirit of it, especially in adapting it in the light of the teachings made hereinabove, to the treatment of different forms of articles of the base metal.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent, is:

1. A process of preparing iron or steel for coating with molten metal, which comprises cleaning the iron or steel and coating it with a phosphorus bearing material chosen from a class consisting of a water solution of phosphoric acid, and a water solution, having an acid reaction, of a salt of phosphoric acid, drying the iron or steel so as to leave a coating of phosphorus bearing material on its surfaces, and thereafter heating it in the presence of a reducing atmosphere, at sufficient temperature and for a sufficient length of time to reduce the phosphorus bearing material and to cause phosphorus to be absorbed by the surfaces of the iron or steel.

2. The process of preparing iron or steel for galvanizing which comprises cleaning the iron or steel, evenly coating it with a solution of phosphoric acid, drying the iron or steel while still coated with the phosphoric acid solution, and thereafter heating it in the presence of a reducing atmosphere at a sufficient temperature and for a sufficient length of time to reduce the phosphorus and to cause it to be absorbed by the surfaces of the iron or steel.

3. A process of preparing iron or steel for galvanizing which comprises cleaning the iron or steel and treating it with an acid solution of a phosphoric acid salt, drying the iron or steel without removing the said solution from its surfaces, and thereafter heating it in the presence of a reducing atmosphere, at sufficient temperature and for a sufficient length of time to reduce the phosphorus, and to cause it to be absorbed by the surfaces of the metal.

WILLIAM E. MARSHALL.