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METAL COATING PROCESS AND APPARATUS THEREFOR

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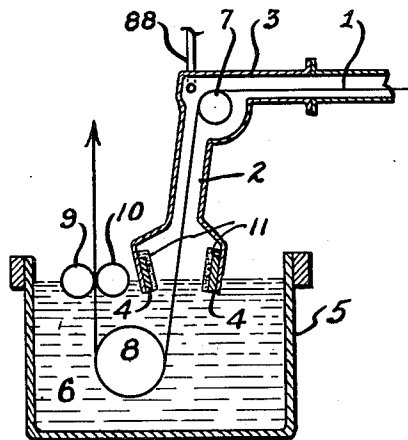


FIG. 1.

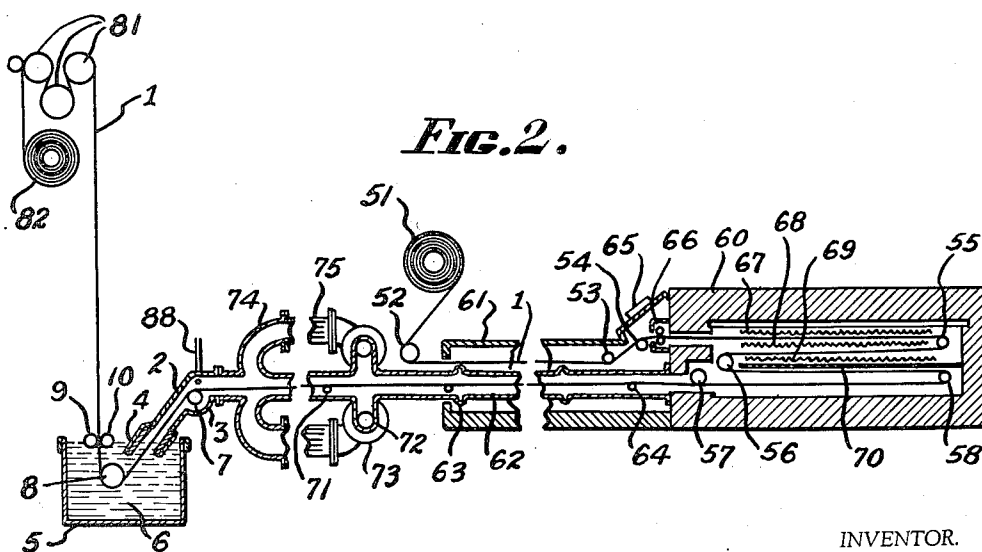


FIG. 2.

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METAL COATING PROCESS AND APPARATUS
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3 Claims. (Cl. 117—51)

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This invention relates to a process of continuously coating metallic objects with another metal, in which the objects pass through a reducing treatment at annealing temperature which is followed by a cooling of said objects in a protective atmosphere free from oxygen and then brought in contact with the coating metal in a molten state.

This process is disclosed in my Patents Nos. 2,110,893 and 2,136,957. In particular, in this last patent I described methods of chemically binding traces of oxygen either free or in certain combinations, such as water vapor, which may be present in the protective atmosphere of the cooling chamber, through which the objects to be coated are passed before entering into the molten coating bath. Such methods essentially consist in providing within said cooling chamber free surfaces of bodies having a high affinity for oxygen, such as certain molten metals, and also providing means for a constant removal of products of reaction.

In this application, I disclose a method by which such a deoxidation may be produced in a very advantageous way without the introduction of any special devices for this purpose, by so arranging and operating the main apparatus as to enable a certain quantity of vapor of the coating metal or metals to be generated on the free surface of the bath enclosed by the cooling chamber, and circulated in that portion of the cooling chamber where the presence of even a small quantity of oxygen, either free or in certain gaseous combination, is detrimental to the process of coating. Such vapor has, under the conditions of temperature and pressure prevailing, a very much higher affinity for oxygen than the free-exposed surfaces of the object to-be-coated, and therefore it gradually becomes oxidized and is deposited in the form of a fine powder, as metallic oxide, on the walls of the cooling chamber.

It is a question here of removing only minute quantities of oxygen either free or in the form of water vapor, that finds its way into the cooling chamber, partly by diffusion from the high temperature part of the furnace, partly through joints between the various parts of the cooling chamber, and partly even from the gas supplied to form the protective atmosphere. The quantities, however, are very small, and the thickness of such metallic oxide deposits on the walls of the chamber, rarely exceeds $\frac{1}{8}$ ", after a month or more of a continuous operation of a unit.

My improved process is also very valuable when

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it comes to a composite treatment of cold-reduced steel, such as strip or wire, which consists in removing residues of lubricant from the surface by pre-heating in an oxidizing atmosphere, annealing or normalizing the metal in a reducing atmosphere, and cooling it so as to obtain the required degree of softness and pliability, always under a protective atmosphere, and subsequently applying a tightly adhering metallic coating of such metals as zinc, tin, aluminum, copper, etc. by bringing it in contact with such metals in molten condition. Such coating must be, in many cases, ductile and adherent sufficiently to permit certain forming or drawing operations to be performed afterwards.

Not only can all those operations be conveniently performed in one continuous unit which is easy to control and keep in uninterrupted operation, but certain other advantages are obtained, as will be clear later.

I prefer to explain the principle of this invention by means of a drawing, of which

Fig. 1 represents the metallizing pot in cross section together with a corresponding portion of the cooling chamber or hood, and the necessary guiding and exit rolls.

Fig. 2 represents also in schematic longitudinal section, the whole unit, inclusive of the pre-heating and the normalizing furnaces, of the regenerative horizontal type, the pre-cooling chamber with a metallizing pot roughly as on Fig. 1.

In Fig. 1, the metallic (for instance zinc) bath 5 is contained in the pot 5, and the metallic object to-be-coated, for instance steel strip 1, passes from the horizontal portion of the cooling chamber 3, over the roll 7, into the inclined portion 2, therefrom into the metallic bath 6, over roll 8, and up through exit-rolls 9 and 10, situated substantially at the upper level of the metallic bath, from which point the cooling and solidifying of the metallic coating begins. Means for pulling the strip at a certain speed through the unit are not shown here.

As has been disclosed in my U. S. Patent 2,136,957, above referred to, and for the purpose of obtaining a better coating, I prefer maintaining the coating bath at a temperature above, but not greatly above, the melting point of the coating metal. On the other hand, the metallic vapor I require for the purpose described is generated in the desired proportion at a temperature higher than the one mentioned. But, as it is explained in the same patent, the metallic strip 1 should,

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at the point of its entry into the metallic bath, have a temperature of between 20 and 80° C. higher than the latter. I therefore provide the bell-shaped downward portion 2 of the cooling chamber of a certain height, not less than about 1½ or 2 feet, ending with sealing lips 4, which enter into the coating bath, and which I make slightly wider than the rest of the cooling chamber, so that the distance between the strip 1 and the lips 4 is roughly 6 to 10".

In this way, by the excess heat contained in the strip 1, a pool of molten coating metal of a higher temperature than the rest of the bath 6 will gradually form itself at or near the spot where the strip enters into the coating bath 6. The broadening of that part of the cooling chamber at 4 increases the free evaporating surface of the metal and also places the lips 4 a little bit away of the point of highest temperature, so that the molten metal does not dissolve them so rapidly. For the same purpose, I make them of a heavier gauge of metal to increase their life, and also protect them, for certain coating metals, with a baked-on enamel.

I put around the inner side of that bell-shaped cooling chamber 4, a refractory lining 11, the heat insulating property of which is very valuable in maintaining that temperature gradient as between the relatively hot portion of the bath within the bell-shaped hood 4, and the rest of the bath 6.

Heating elements may be provided, within such refractory lining if it is required to raise the temperature of this hot pool still higher. Such heating elements are also valuable for starting the unit from a cold condition. A layer of a heat-insulating material may be interposed between the refractory lining and the metallic lips 4.

I also found that by making the portion 2 of the cooling chamber not quite vertical, but at an angle, so that the strip 1 enters the coating bath at this angle which usually is between 60 and 80°, still better results are obtained because the hot object passing into the coating bath comes into contact with the superficial layers of the bath with greater surface contact in a given depth, and therefore gives up more heat to the enclosed surface of the bath than if it passed into it vertically. Thus the said enclosed surface of the coating bath evaporates more readily.

The diffusion of those metallic vapors towards more remote portions of the cooling chamber takes place in the natural way. I prefer, however, to increase its rate by admitting the fresh supply of the reducing gas not into the heating or annealing furnace, but into the cooling chamber, and at a spot fairly close to the molten metal bath, so that it will create a certain small amount of gas movement within the inclined portion 2 of the cooling chamber, and will carry the metallic fumes towards the hotter portions of the cooling chamber. Any amount of oxygen or oxygen-bearing gases or vapors carried with the fresh reducing gas supplied will thus be immediately bound and thrown out as metallic oxide powder by the presence of said metallic fumes, as will any infiltration of outside air or penetration of contaminated gases by diffusion from the furnace situated at the other end of the cooling chamber.

It must be clearly understood that it is a question of relatively small quantities of oxygen present and that for this purpose I prefer to use a unit where the entrance end of the furnace is fitted with an effective gas seal. In such case,

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the amount of fresh gases supplied need not be large, say one or two pounds of fresh gases per hour for a unit capable of coating three tons of strip per hour, and herein lies another advantage, as this permits me to obtain just the right kind of gas flow.

I found that the resulting coating is still further improved and rendered immune to slight variations in temperatures, when I use, as a reducing gas, a mixture of hydrogen and nitrogen with a small quantity of ammonia, such as when anhydrous ammonia gas, NH₃, is passed through a heated iron chamber and almost completely dissociated into its component gases. I prefer to leave about ½ to 1% of undissociated ammonia gas in the mixture, but I found that even much smaller quantities bring about very desirable results.

One of such results is that a fairly good adherence of a zinc coating can be obtained for example even when the strip to-be-coated is immersed into the molten spelter bath at roughly the same or even a lower temperature than the temperature of the bath.

One of the characteristic features of this process is that it does not require any time to obtain a satisfactory coating, both as regards adherence and weight. In the regular process of wire galvanizing, for example, the wire has to pass a certain distance within the spelter bath which may be 40 or even 60 ft. long. In other words, with the old processes, a certain amount of time is necessary for the flux to act upon the surface of the base metal in order to form the well-known alloy of the base with the coating metal. Contrary to this, with my process, the duration of the actual "wetting" of the strip is nil. Such an instantaneous "wetting" of the metal allows me, as disclosed in one feature of my Patent 2,136,957 to galvanize a steel strip by letting it pass first through a bath of pure metallic lead, and then through a zinc bath floating upon the first and only 1" deep. The coating obtained is just as good as when passing through a bath consisting of zinc only, where for obvious reasons, the minimum travel of the strip in zinc is much longer.

Fig. 2 shows a complete unit for degreasing, normalizing, cooling and coating of a strip and shows some further advantages that are derived of the present invention.

The steel strip 1 is unreel from coil 51 and passes over pulley 52 into the preheating chamber 61, where any adhering remainder of lubricant is burned away and a thin uniform film of metallic oxide is formed.

Strip 1 then passes over pulleys 53 and 54 and under cover 65, through seal 66 into the furnace 60, which may be preferably electrically heated, as by resistors 67, 68 and 69, or by gas-heated radiant tubes or other means. The strip while being heated passes over pulleys 55 and 56 into the lower part of the furnace housing, under the insulating wall 70 and over pulley 58. In this portion, the strip has already attained its full annealing or normalizing temperature, as the case may be, and the temperature is allowed to go down slightly.

Strip 1 then passes the recuperative cooling chamber 62, preferably made of a heat-resisting steel and as gas-tight as the furnace itself. The chamber may be fitted with bulges 63 to compensate for dilatation. In this chamber the temperature of the strip 1 is allowed to go down at a higher rate of speed, while, at the same time, the heat liberated is used to preheat, by direct

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radiation of the cooling chamber 52, which is insulated from the bottom, the entering strip 1, as explained above, resulting in an important saving.

For certain materials such long cooling period is not needed, and, in such cases, the strip 1 may be passed from pulley 56 direct under pulley 57 and avoiding pulley 58.

On passing to the second part 71 of the cooling chamber, strip 1 is cooled, when required, also by convection of gases which are moved in counterflow being circulated by fans 73, drawing gases from chamber 71 through tubes 72 and returning them over pipes 74, which may contain water-cooled pipes 75, back into the cooling chamber 71, but preferably so as to impart to them a certain velocity against the direction of the motion of strip 1, as by suitably inclining the exit or exits of the circulating pipes 74, as shown on Fig. 3, so that the cooling gases move in counterflow to the movement of the strip. This cooling is preferably brought to such point that the strip 1, after passing over pulley 7, dips into the molten bath of coating metal 6 contained in pot 5, while still at a temperature of 20 to 80° C. above the temperature of the latter.

The strip then passes under roll 8 and between exit rolls 9 and 10 into the atmosphere where it cools down and is propelled by a driven group of rolls 81 and coiled up by reel 82.

According to the present invention, during operation of the unit, the reducing gases contained in portion 2 of the cooling chamber are more or less stationary except for a certain amount of circulating motion imparted to them by the fresh gas admitted at 88. They contain or carry a certain amount of the vapors of the coating metal and also of a finely divided metallic powder in various stages of oxidation. A part of the oxides may be deposited on the walls of cooling chamber 2. In many cases and for the purpose of increasing the deoxidizing power of such metallic vapors in the cooling chamber, I add to the coating metal a slight percentage of such metal, metals, or even non-metallic oxidizable constituents, which have a higher affinity for oxygen than the coating metal and are, at the same time, not detrimental to the structure of the coating. Such added ingredients may be more volatile than the coating metal and the deoxidizing metallic or other vapors shall contain a much higher percentage of additional metal than the coating bath. Thus, with a proper choice of such additional metal, or other ingredients, I can, in certain cases, very greatly increase the deoxidizing power of the metallic vapors in the cooling chamber above the molten coating metal. For instance, a bath of spelter containing only .2% of aluminum may produce, as a result of deoxidation of the atmosphere in the cooling chamber, a metallic oxide deposit, which contains up to 20-30% of aluminum oxide. It is to be remarked that not only is such a small addition of aluminum in the coating bath not detrimental to the structure of the coating, but on the contrary, it presents many advantages in improving the quality of the coating as is disclosed in my copending application U. S. 138,432, now Patent No. 2,197,622, issued April 16, 1940.

Strangely enough I find that a small addition of aluminum in the presence of some percentage of tin in the bath of spelter produces a deposit of oxides containing zinc, aluminum and tin oxides in about equal parts.

Beyond the portion 2 of the cooling chamber, the gases move steadily towards the furnace 60,

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as fresh supplies are pumped in at 88, which may be the only point, although it may be advisable to also furnish fresh reducing gas at other points of the unit.

In the cooling chamber 71, which contains the convection cooling system above described, the gases become intimately mixed with the metallic vapors and with the fresh gas supplied which insures that the chemical binding of whatever oxygen is left in this space is carried out to the limit of chemical equilibrium which is just sufficient to preserve the surface of the strip 1 in condition for the coating. Without such mixing effect, some parts of the strip, where the diffusion would not act quite enough, might be subject to the action of gases still containing oxygen in some form and such surfaces would not be prepared to take a perfect coating, on dipping in the molten metal bath. In most cases, the last part of chamber 71 is the place where the comparatively low temperature of the strip makes it most vulnerable in presence of small amounts of oxygen under the special conditions of chemical equilibrium in presence of gases and vapors, as above set forth.

As the reducing gases move along further, into the chamber 71 towards the furnace, they meet, by diffusion, ever increasing amounts of contaminated gases from the furnace 60. Owing partly to the reduction of the oxide film on the strip, and partly to infiltration and other reasons, such gases carry bigger quantities of oxygen, chiefly in the form of H₂O, and to a lesser extent of CO, especially if some other kind of a protective gas is introduced into the furnace.

The present invention permits an easy control of the quantity of metallic oxides carried by the reducing gases and thereby takes advantage of the fact that the vulnerability of the strip in the presence of small quantities of oxygen gradually diminishes in the forward portion of the cooling chamber 71, where the strip still has a high temperature. It is advantageous, when applying the present process, to carry only such quantities of metal vapors that they be almost completely oxidized about half-way in the cooling chamber, so as not to introduce any metallic vapors into the furnace 60, where they could be deposited on the heating resistors and other metallic parts, and cause their rapid corrosion and failure.

Such destruction also invariably follows, especially when using resistors containing mostly nickel and chromium, if a part of the oxides generated in the cooling chamber are not deposited there but are carried into the furnace. Therefore, the arrangement according to the present invention, where the lower part of the furnace 60 is in reality the first part of the cooling chamber and does not need to have any heating elements, is extremely advantageous from the point of view of safety of operation of such unit and freedom from breakdowns, as the gases are given a further chance to deposit whatever may still be carried of the metallic oxides, in this lower part of the furnace 60, before they come in contact with the resistors. This is further facilitated by the fact that the velocity of the gases is further reduced owing to the increased volume and section of this furnace chamber in comparison with the cooling chamber.

The pre-cooling chamber situated in the lower part of the normalizing furnace 60 also gives other, purely metallurgical advantages, in that it permits an easy and economical way of soaking the strip, after it has reached the usual annealing

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or normalizing temperatures, mostly around 850° to 950° C. for low-carbon steel, while permitting it, at the same time, to have a definite although very slight downward gradient of temperature. Such conditions are instrumental, in view of preceding cold reduction, in obtaining the greatest possible grain growth of the metal in the least possible space of time.

With the subsequent cooling, at a somewhat quicker rate, in the cooling chamber 71, followed by a relatively fast cooling only in the latter portion of said chamber 71, i. e. where the strip enters at a dull-red heat, conditions are obtained where a strip is annealed pretty nearly as soft as if it had been subjected to a box-anneal, but has much better deep-drawing properties.

Thus two important advantages: (1) complete scavenging of oxygen in the dangerous zones of the cooling chamber, and (2) a much more appropriate cooling cycle, are accomplished at the same time.

Another advantage is that the furnace 60 is relatively small and has a lesser surface to be heat-insulated.

This furnace has been described by way of example only, as evidently other types may be used, such as vertical, inclined, recuperative or non-recuperative furnaces.

I claim:

1. In apparatus for the purpose described, a bath of molten metal, an elongated chamber through which heated strip metal to be coated is passed, means for maintaining in said chamber a non-oxidizing atmosphere, a connection between said chamber and said bath having a portion entering said bath, said last mentioned portion being enlarged as respects the body of said connection and provided with lips at the portion entering the bath of heat insulating character whereby to isolate and insulate a portion of said

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bath which may be maintained at a higher temperature than the remainder of said bath.

2. In apparatus of the character described, a chamber containing a non-oxidizing atmosphere through which heated metal to be coated can be passed for cooling, a bath of molten metal, a connection between said chamber and said bath through which said metal to be coated may be passed in leading it into said bath, and heat insulative means forming part of said connection and extending into said bath for isolating a portion of said bath which may be maintained at a temperature higher than the remainder of the bath for promoting vaporization of metal from the surface of said isolated portion, and means in connection with said chamber for promoting a movement of gas therein to assist in the dissemination of said vapors.

3. In a process of coating metallic strip by contacting it with molten metal, wherein the strip is passed through a confining chamber provided with an entrance portion extending downwardly into the molten bath and containing a reducing atmosphere and under operating conditions a small amount of active oxygen, and wherein the strip is passed into the bath of molten coating metal while the strip is protected by said atmosphere, the step of increasing the evaporation of metal vapors from the surface of said bath so as to scavenge said atmosphere of active oxygen by chemically combining it with such metallic vapors, which comprises isolating and insulating the entrance portion of said bath, and heating the atmosphere adjacent the surface of said bath and the upper layer thereof which is within the said entrance portion, thereby maintaining the temperature in said entrance portion materially higher than the temperature elsewhere in said bath.

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