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COATED IRON OR STEEL ARTICLE AND METHOD OF MAKING THE SAME

No Drawing.

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This invention has reference to a zinc-coated iron or steel article and to the process of producing such an article, which consists in subjecting the article base to a phosphorizing medium at a temperature and for a period of time sufficient to produce a thin surface layer of high phosphorus content as an integral part of said base, and subsequently zinc-coating said base by the hot-dip galvanizing process.

The invention comprehends primarily the producing of galvanized wire, particularly for telephone and other electrical transmission lines; although the invention may be found useful in the coating of other iron or steel articles as, for example, sheets, strips and the like.

In the application of the invention to the hot-dip galvanizing of wire it is aimed to produce a wire with a tightly adherent coating on a "low phosphorus" steel base which will withstand severe bending without peeling or flaking of the coating from the base wire, especially in instances where it is found necessary to wrap the wire around its own diameter and for splicing and other deforming usage. Furthermore, in the utilization of the invention, particularly for telephone wire, a zinc-coated wire is obtained with better physical and electrical properties than those found in telephone wire manufactured from "high phosphorus" steel.

In the practice of the invention, when applied to the zinc-coating of wire, the base wire of any suitable gauge is treated at an elevated temperature in an atmosphere of phosphine (PH_3) gas whereby the phosphorus content of the surface layer of the base wire is increased. This phosphorizing action occurs when the phosphine gas comes in contact with the surface of the hot base wire whereby it is dissociated into its elements phosphorus and hydrogen, the phosphorus atoms being physically absorbed in the surface layer of the base wire. While we have described the dissociation of the phosphine gas at the surface of the hot wire, this is not essential to the practice of the invention as the hot wire could easily be phosphorized by the physical absorption of

phosphorus atoms into its surface layer from a gaseous mixture of phosphorus and some non-oxidizing gas such as hydrogen. In any case such phosphorizing action could be a physical reaction, that is, the physical absorption or solid solution or diffusion of phosphorus atoms into the surface layer of the steel base.

The temperature at which the wire is phosphorized may be sufficient to simultaneously anneal it, and we prefer to take advantage of this effect; however, we realize that the annealing treatment may be accomplished either before or after such phosphorizing treatment. When the phosphorized base wire is subsequently galvanized a wire is produced with a heavy and tightly adherent zinc coating which will withstand severe bending and forming without flaking or peeling of the zinc coating.

In the application of the zinc to such phosphorized base wire the coating may be applied in the usual manner for producing heavily coated galvanized wire. Experience has demonstrated that very effective and unusually satisfactory zinc coatings may be obtained by the use of the ordinary method of hot-dip galvanizing when applying the zinc to the phosphorized surface of the iron-base body resulting in obtaining a tightly adhering heavy zinc coating on such a conditioned surface. However, practice may determine that zinc coatings (fully as adherent) may be applied to the phosphorized surface of the ferrous base by other methods of zinc coating wherein an alloying action between the zinc and the ferrous base takes place.

We are aware that in the production of open or rimmed steel phosphorus is added to the molten steel to make it possible to obtain an adherent zinc coating by galvanizing articles made from such steel. The presence of the added phosphorus in telephone wire, made from such steel, is disadvantageous because it increases the electrical resistance and the hardness of the base wire. Our invention will eliminate the necessity for additions of phosphorus to the molten steel, which is to be subsequently galvanized,

the phosphorus being introduced only into the surface layer of the solid steel, preferably in the drawn wire, although it may be introduced into the surface layer of the solid steel at any time after its solidification in the ingot mold; therefore, we are able to obtain the beneficial effects of the presence of phosphorus in the surface layer of the steel during galvanizing at the same time avoiding the detrimental effect of phosphorus on the electrical and physical properties of the steel base such as electrical resistance, tensile strength and elongation.

As one example of the use of the invention we will describe the production of zinc coated telephone wire as follows:

The cold drawn wire first having been drawn to the desired gauge is preferably passed through the usual muriatic acid bath for cleaning, then is passed through a water bath to wash off the iron chloride and muriatic acid. The cleaned wire is then passed through an annealing chamber containing phosphine gas. From the annealing chamber the wire is passed, without contact with the air, directly into the molten zinc bath. The wire leaves the zinc bath preferably in a vertical direction through the usual charcoal cover and after cooling is coiled on take-up blocks.

In our preferred practice the annealing chamber is sealed on the entering end with a fluid seal; the exit end of said chamber is sealed by having that end immersed in a molten zinc bath.

We have found that we are able to simultaneously anneal the wire and cause the dissociation of the phosphine into its elements.

The hot wire being in contact with the phosphine, dissociates the phosphine, the wire physically absorbing the phosphorus atoms in the surface layer. We have found that this action may be made to take place at different temperatures but we prefer to use a temperature ranging from 1250 to 1350 degrees F. Through this temperature range we are able to both anneal and to phosphorize the surface layer of the wire. By passing the hot phosphorized wire directly into the molten zinc bath without contact with air, we are able to obtain a greater bonding and alloying action between the iron or steel base and the zinc coating.

The depth of penetration of the phosphorus into the steel is dependent upon the rate at which the wire passes through the annealing chamber, the length of annealing chamber and the temperature thereof. We have found it sufficient and desirable to limit the time of phosphorizing to a relatively short period so as to obtain only a thin phosphorized surface layer.

By "phosphorizing" we mean the addition of small quantities of the element phosphorus and no other element into the surface

layer of the steel base. It is this element phosphorus alone which so affects the properties of the surface layer of the steel base as to cause the formation of a strongly adherent zinc coating when the steel base is subjected to galvanizing. Therefore, in the practice of our invention we add only phosphorus to the surface layer of the steel base and do not form a superficial iron phosphate coating as in the rust-proofing processes commonly known as "Parkerizing", etc.

We are aware that "phosphorizing", that is, the addition of phosphorus to the surface layer of a steel article, is not new and has been used to produce a rust-proof condition or coating on the surface of the steel article. In practicing our invention we do not use the addition of phosphorus to the surface layer of the steel base for rust-proofing, but use it to obtain a strong bond between the steel base and the zinc coating applied thereto. It should be pointed out that in the practice of adding phosphorus to the surface layer of the steel base for rust-proofing purposes the steel article is allowed to remain in contact with the phosphorizing medium for a long period of time in order to produce a thick phosphorized surface layer. We differ from the last foregoing in that it is important that the steel wire be allowed to remain in contact with the phosphorizing medium for only a relatively short period of time, so as to produce only a very thin phosphorized surface layer, in this way to so condition the surface layer of the steel wire so as to effect a strong bond between the steel base and the zinc coating. It is emphasized that the adding of phosphorus to the surface layer of a steel wire and the applying of the zinc coating to the so conditioned surface is a continuous process. We desire to be understood that we do not add the phosphorus to the surface layer of the wire for increasing the rust resisting qualities of the wire. The phosphorized surface layer we produce is so very thin that the rust resisting properties of the wire are not appreciably increased. The very thin phosphorized layer is only used as a means of increasing the adhesion or cohesion between the steel base and the zinc coating. The zinc-coated wire so produced, as heretofore pointed out, is capable of withstanding sever bending or forming such as bending around its own diameter without flaking or peeling of the zinc coating.

As an alternative procedure we have found that very good results may be obtained by first passing the wire through an annealing chamber containing phosphine and then subsequently cooling the phosphorized wire, then cleaning it in an acid bath. The clean phosphorized wire is then passed through a water bath and the usual flux and finally subjected to the coating bath of molten zinc.

While we have discussed the use of phosphine gas as a phosphorizing medium, it is to be understood that any compound of phosphorus, either gaseous, liquid or solid which at elevated temperatures will dissociate to give free phosphorus atoms or molecules which in turn would be physically absorbed by the surface layer of the hot iron or steel base may be used as a phosphorizing medium.

While we have described in connection with the invention the use of zinc as a protective coating on a phosphorized iron or steel article, we have in mind that other coatings may be used as, for example, lead, tin, cadmium, copper, nickel or aluminum, etc.

The terms and expressions which we have employed are used as terms of description and not of limitation and we have no intention in the use of such terms and expressions, of excluding any equivalent for the features shown and described, but recognize that various modifications are possible within the scope of the invention claimed.

What we claim is:

1. A zinc-coated iron or steel article, comprising a ferrous base, which has as an integral part of the base a phosphorized superficial layer containing phosphorus in excess of that contained in the interior of the article base, and a coating of zinc alloyed to said phosphorized surface.

2. The process of zinc-coating an iron or steel article, which consists in subjecting the article base to an atmosphere of phosphine at a temperature and for a period of time sufficient to produce a thin surface layer of high phosphorus content as an integral part of said base, and subsequently zinc coating said base by the hot-dip galvanizing process.

3. The process of zinc-coating an iron or steel article, which consists in subjecting the article base to a phosphorizing medium at a temperature and for a period of time sufficient to produce a thin surface layer of high phosphorus content as an integral part of said base, and subsequently zinc-coating said base by the hot-dip galvanizing process.

4. The process of zinc-coating an iron or steel article, which consists in subjecting the article base to a phosphorizing medium at a temperature and for a period of time sufficient to produce a thin surface layer of high phosphorous content as an integral part of said base, and subsequently zinc-coating said base by passing it directly into molten zinc without contact with air.

5. The process of zinc-coating an iron or steel article, which consists in annealing said article and during such annealing to simultaneously produce a thin surface layer of high phosphorous content as an integral part of said base, and zinc-coating said article by passing it directly into molten zinc with-

out the article cooling or coming into contact with air.

6. The process of continuously zinc-coating iron or steel wire, which consists in annealing the base wire and during such annealing to simultaneously produce a thin surface layer of high phosphorous content as an integral part of said wire, and immediately zinc-coating said wire by passing it directly through a bath of molten zinc without the wire cooling or coming into contact with air.

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