Feb. 18, 1941. U. C. TAINTON 2,231,967

ZINC COATED ARTICLE

Filed April 24, 1937

Fig. 1.

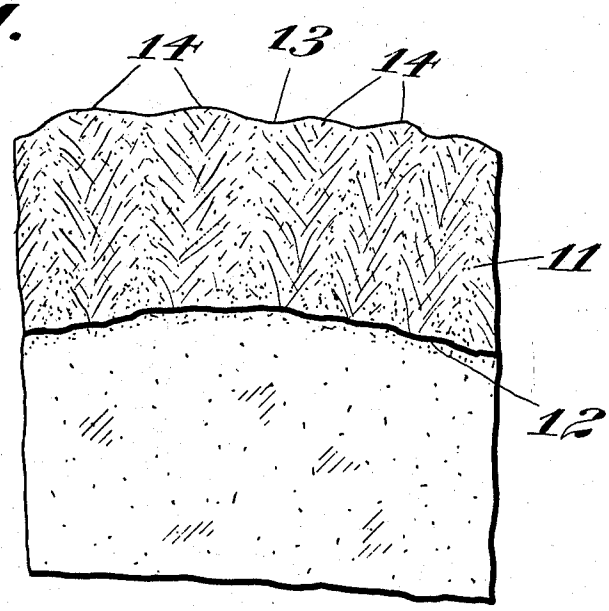
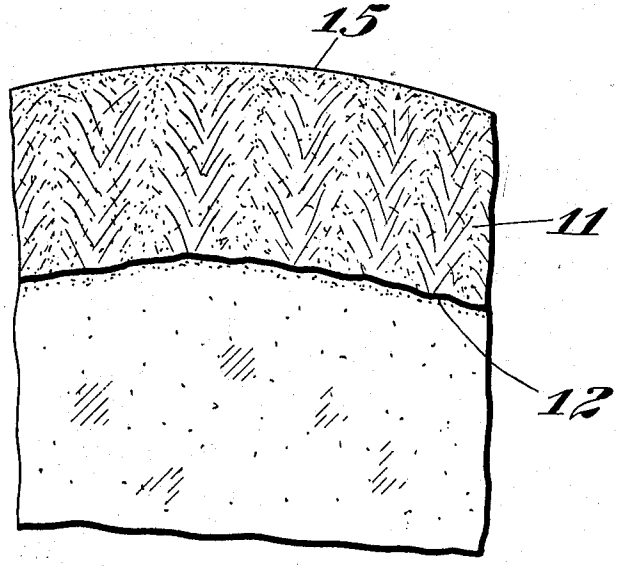


Fig. 2.



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ZINC COATED ARTICLE

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Application April 24, 1937, Serial No. 138,825

2 Claims. (Cl. 204—55)

This application is a continuation in part of application Serial No. 600,577, filed March 22, 1932.

My invention relates to ferrous articles coated with zinc, and has for its object the provision, as a new article of manufacture and commerce, of an improved zinc-coated ferrous article.

Of the many forms of protection that have been used for the preservation of ferrous surfaces, such as iron, steel, etc., none is so satisfactory in point of permanence and economy as that afforded by a layer of zinc. At the present time there are two distinct types of zinc-coated ferrous articles. By far the most important, in point of volume of production, is the type produced by the so called "hot dip" process of galvanizing. The second type, that produced by electro-plating, has heretofore been produced to but a limited extent and for special purposes.

Each of these two types of product has heretofore involved certain more or less marked disadvantages. Galvanized coatings, produced by the hot dip method, are brittle. The so called "zinc coating" is not a true zinc coating at all, being, in fact, a zinc-iron alloy which is brittle and which is not nearly so resistant to corrosion as elemental zinc itself.

Galvanized articles, of the hot dip variety, are produced by immersing iron or steel bodies in a molten bath of zinc. The coating thus produced is a heterogeneous combination of different alloys of zinc and iron. Photomicrographs of this type of coating reveal the existence of at least two and sometimes three distinct layers. Next to the ferrous metal there is a layer which consists mainly of the intermetallic compound $FeZn_3$; the outermost layer is practically a saturated solution of iron in zinc. At times there is an intermediate layer consisting of the intermetallic compound $FeZn_7$.

When galvanized articles, produced by the hot dip method, are bent, the coatings show a marked tendency to crack and peel. Various attempts have been made to improve the mechanical properties by annealing operations. This tends to decrease the degree of stratification but bending still produces numerous fine cracks.

The type of galvanized bodies produced by electrolysis possess certain distinct advantages over the hot dip product. The coatings of zinc frequently have a high degree of purity and therefore have much higher ductility and with far less tendency to crack or peel. Moreover, the greater purity of the zinc contributes considerably greater degree of resistance to corrosion.

Nevertheless, the electro-galvanized variety has heretofore offered but little competition to the hot dip product. In the first place it is considerably more expensive to produce than the hot dip article. The structure of the coating which has heretofore been considered to be essential can only be produced by slow operations. Furthermore, the structure demanded is such that it is practically impossible to produce coatings of a substantial degree of thickness by a practical and commercial operation. In spite of the inherent defects of the hot dip article, coatings of substantial thickness have always been produced by the hot dip operation.

Heretofore it has always been believed to be essential that the coatings, electrolytically produced, be of exceedingly fine grain metal. The idea has been to produce such grain size that the metal is essentially in the amorphous condition. The practice, prior to applicant's present invention, has always been to deposit the metal under such conditions as to avoid a continuing growth of the crystals. Every effort was made to have as large a number as possible of nuclei of deposition and as far as possible to prevent the growth of the separate grains. This prior art structure necessitated the use of processes which were decidedly limited in rapidity of deposition. The prior art conception of what was essential in coating structure effectively prevented the development of processes which were sufficiently rapid to produce satisfactory coatings of considerable thickness. The prior art processes, in practice, were limited to operations which were too slow to produce coatings which could compete in cost with coatings of the hot dip type. In practice, coatings of substantial thicknesses were always produced by the hot dip method.

This applicant has discovered that the prior workers in the art were in error as to what was essential in obtaining the best type of electrodeposited zinc coatings. He has discovered that the structure of the coating should be essentially different from that heretofore considered to be essential. The new type of coating which he has discovered and developed forms the subject matter of the present application.

Applicant seeks and obtains a coating of a coarsely crystalline structure. His coating consists of crystals which are substantially continuous from the ferrous surface to the outer surface of the coating.

In producing his coatings he seeks to cause a continuous and uninterrupted growth of the crystals, such growth continuing until the coating

is completed. All of the conditions of his operation are maintained with the end in mind that nothing be allowed to interfere with the crystal growth once it has commenced.

Referring to Fig. 1 of the drawing, the coating 11 is shown as deposited on the ferrous surface 12. Coating 11 comprises crystals which are deposited in column-like formation approximately normal to the ferrous surface. The crystals, as will be readily evident, are substantially continuous, or uninterrupted, from the ferrous surface 12 to the outer face 13 of the coating.

My preferred method for producing these coatings involves the use of electrolytes of zinc salts containing a high percentage of free acid. For example, in using an electrolyte containing zinc sulphate, I prefer to have free sulphuric acid of a content between 20% and 30%. I prefer to use insoluble anodes and I employ high current densities, several hundred amperes per square foot of cathode surface. In the case of wire, for example, I employ current densities between 700 and 2,000 amperes per square foot of cathode surface.

Before plating, the ferrous article should be subjected to an effective cleaning operation and care should be taken that the ferrous body is free from occluded hydrogen. This result may be effected by subjecting the article as anode in an acid electrolyte to a current density sufficiently high to render the iron passive. The electrolyte, during this operation, should contain 10% or more of free acid and the current density should be 100 or more amperes per square foot of cathode surface. Sulphuric acid is satisfactory for this purpose. Immediately following this treatment the ferrous article is passed into the plating electrolyte. It is important that the plating operation be instituted immediately upon the entry of the article into the free acid containing electrolyte to prevent hydrogen being occluded before plating is commenced.

Applicant now desires to call attention to those conditions of operation which he has found effective in producing the continuous growth of the crystals of the coating. First of all, he avoids those conditions which were employed in the prior art practices for insuring a finely granular structure. One of the means most frequently employed by the prior art was the use of agents for preventing grain growth. For example, it has been common practice to employ small amounts of organic colloids, such as gelatine, which would be deposited in very small amounts with the metal and would protect the metal from grain growth by forming a sheath around the grains. In my practice I avoid the presence in the electrolyte of appreciable quantities of organic colloids. Preferably, organic colloids should be absent. In any case the organic colloids present in the electrolyte should be in amounts insufficient to prevent the desired crystalline growth.

The presence of various other substances than organic colloids in the electrolyte also acts to prevent a free crystal growth. For example, relatively small amounts of lead in the electrolyte would cause the deposition of minute amounts of lead in the zinc coating and prevent the free growth of the crystals. Heretofore, in those electrogalvanizing processes where so called insoluble anodes have been used, the anodes most frequently have been made of lead. When ordinary lead anodes are used, they are slowly disintegrated giving sufficient lead to the electrolyte to prevent free crystal growth. In my operation I use such anodes as will introduce insufficient lead into the electrolyte to cause this inhibition of crystal growth. For example, I use with success anodes of lead and silver such as are disclosed in my U. S. Patent, Serial No. 1,759,493. Other anodes may be used with high current densities which will not introduce such substances into the electrolyte as will interfere with the desired crystal growth. For example, anodes of densified manganese dioxide may be successfully used.

In preparing the zinc bearing electrolyte I avoid the presence of such substances, frequently associated with zinc, as would interfere with the crystal growth. For example, cadmium is frequently present in zinc bearing electrolytes. In my operation the electrolyte should be prepared from cadmium free zinc bearing material or the electrolyte should be purified to remove all but inappreciable amounts of this metal. The cadmium content must be kept sufficiently low to prevent any interference with the free development of the zinc crystals.

Where the zinc bearing electrolyte is prepared from ore, I prefer to use the purifying process set forth in applicant's patent, Serial No. 1,920,442, granted August 1, 1933.

Applicant's zinc coatings are purer than those heretofore produced, but this is not his distinguishing feature over the prior art. Even in the prior art deposits it was not unusual to obtain a highly pure zinc, the deposited colloidal and other grain growth interfering substances not usually being present in such amounts as to greatly modify the percentage of purity of the deposit. Applicant's coating is essentially different from the prior art coatings in the crystal structure which has been outlined above. Merely insuring a pure deposit does not necessarily mean the production of applicant's structure.

There are other conditions than the deposition of foreign substances which interrupt crystal growth and which applicant must avoid in order to get his desired product. For example, it is common in the art, for the purpose of getting a moderately thick coating, to pass the ferrous body repeatedly through the plating tank. Each time that the article leaves the tank the crystal growth is stopped, resulting in the production of a laminated deposit. In my operation I avoid the repassing of the ferrous article into the electrolyte, employing sufficiently high current density to obtain the desired thickness of coating in a single passage through the electrolyte, thus avoiding the interruption to crystal growth.

Furthermore, I avoid any radical differences in concentration of the electrolyte in different portions of the plating tank, thereby insuring that the composition of the electrolyte does not change the conditions of crystal growth. I have found that if the current densities fluctuate widely, or if the current densities vary substantially in different parts of the electrolytic tank, or if the electrolyte is substantially different in different parts of the tank, the crystal growth may be interrupted.

Preferably, I employ small amounts of inorganic colloids in my electrolyte. I find silica to be very effective. The desired results may be obtained by using a solution of sodium silicate. Certain other inorganic colloids may be em-

ployed, such, for example, as alumina. These colloids are not deposited with the zinc during the coating operation. They act, however, to enable me to obtain a uniform structure. One of the reasons for the prior art insistence upon finely grain structure is that large crystals have a tendency to be developed irregularly during electro-deposition, causing "trees" and the like. By using a suitable inorganic colloid this tendency may be obviated.

The zinc coatings of my invention possess a surface of a considerable degree of roughness due to the coarse crystalline structure. Fig. 1 shows the columns of crystals projecting at points 14 in the coating surface. The article as thus produced by me may be subjected to various mechanical treatments of a kind to distort the outer projections of the crystals of the coating, thereby to obtain a smooth or polished surface. Application of the proper kind and amount of pressure to effect the smoothing and polishing action may be accomplished in various ways as by subjecting the coated articles to rolling or swaging action. Referring to Fig. 2 of the drawing, the outer portions of the crystals are shown as distorted to "smear" the metal, as it were, to give a smooth surface 15.

My coatings have distinct advantages over those of the prior art. I have found that the crystalline structure characteristic of my invention gives a much higher degree of ductility than ever before produced by zinc coating. Articles with my coatings may be subjected to extreme distortion without cracking and flaking. I do not contend that all of the electro-galvanized coatings of the prior art are lacking in ductility, but I do assert that the continuous crystal coating of my present invention has a considerably higher degree of ductility than those lacking my particular crystalline structure.

A great advantage of my coating resides in the fact that it lends itself to methods of production which are very rapid in the deposition of zinc. I am able to use far higher current densities than were previously employed. As previously pointed out in this specification, I employ current densities as high as 2,000 amperes per square foot of cathode surface in the coating of wire. Fine grain metal structure of coatings, of a satisfactory character, as produced by the prior art, could only be obtained with far lower current densities.

The high speeds of deposition available for the production of my coatings not only greatly reduce the cost but enable me to produce any desired thickness of coating. In the prior practice coatings in excess of 1 oz. of zinc per square foot were always produced, on a practical scale, by means of the hot dip method. Electro-galvanized coatings were universally considered to be exceedingly limited as regards thickness. In my process there is no practical limit to the thickness of the coatings. For example, I may produce coatings far thicker than those produced with the hot dip method, two or three times as thick being easily accomplished. This result is securable in but a single passage of the article being coated through the plating tank.

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

1. A ferrous article having a tenaciously adhering, substantially homogeneous coating of electrodeposited zinc of substantial thickness said coating being coarsely crystalline with the crystals substantially continuous from the ferrous surface to the outside surface of the coating, the axes of the crystal growth being approximately normal to the ferrous surface.

2. A ferrous article having a tenaciously adhering, substantially homogeneous coating of electrodeposited zinc of substantial thickness, said coating being coarsely crystalline with the crystals substantially continuous from the ferrous surface to the outside surface of the coating, the axes of the crystal growth being approximately normal to the ferrous surface, and the outside portion of the crystal growth being distorted to provide a smooth surface.

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