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TO METAL SUBSTRATES
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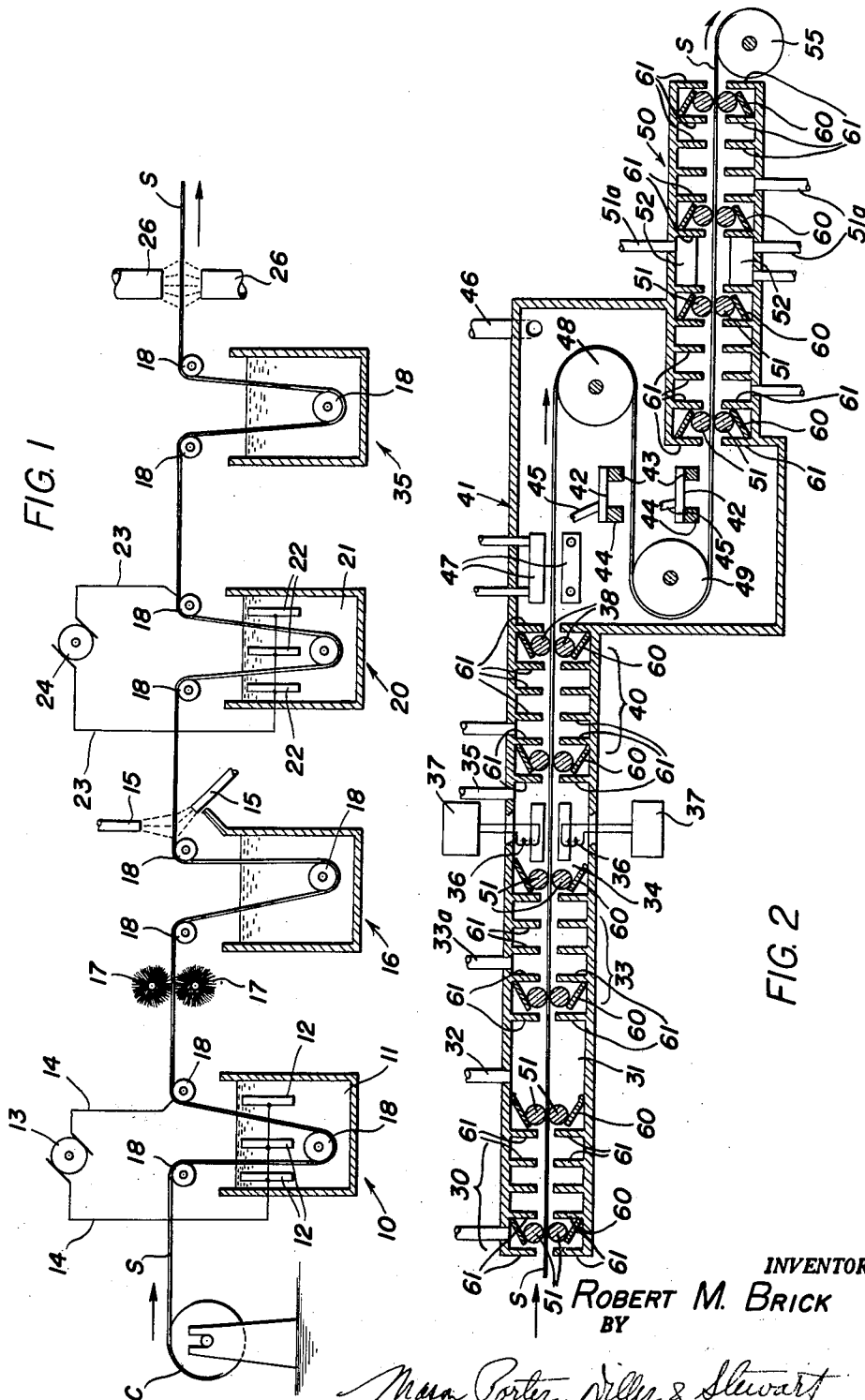


FIG. 2

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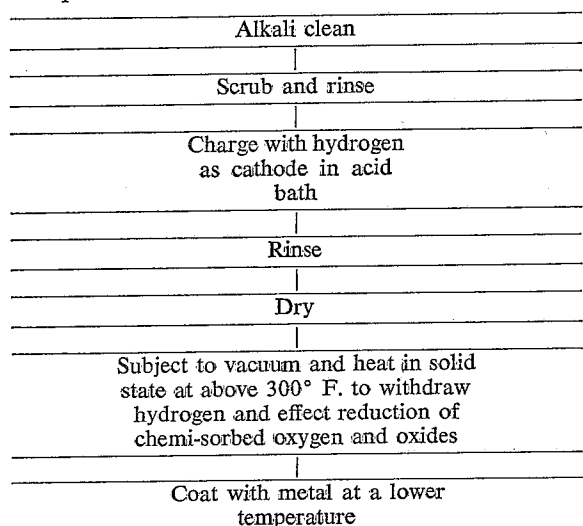
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ART OF BONDING OF VACUUM METALLIZED COATINGS TO METAL SUBSTRATES

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This invention relates to the preparation of coatings upon metal substrates by vacuum deposition of metal thereon from metal vapors, with the production of secure bonding therebetween, and is of particular value in the production of aluminum coatings on ferrous metal, for example in the form of sheets and strips.



Therewith, a composite product can be attained having the advantage of a substrate of a physically strong, cheap and easily fabricated metal but with the metal having disadvantages such as low corrosion or other chemical resistance, with an adherent thin coating of a metal which is nobler and more costly than the substrate but acts to provide the composite with the requisite chemical properties.

It has been proposed to vaporize a metal in vacuo, and effect deposition thereof on a metal sheet as a substrate. In practice, a heating is employed to regularize the coating and improve the bonding effect. With certain pairs of metals for the substrate and the coating, the bonding is accomplished with an interalloying effect at the interface. When steel is coated with deposited aluminum vapor, for example, there is interalloying of body-centered cubic iron and face-centered cubic aluminum. The two metals are so dissimilar electrochemically and in interatomic spacing that such alloying is not a simple intersolution but rather a new phase or phases, i.e., intermetallic compounds, must form. The iron-aluminum alloys such as FeAl₃ and Fe₂Al₅ are hard and brittle so that while bonding can be accomplished in form effective if no mechanical stresses are later to be exerted upon the coated sheet, the relatively thick alloy layers formed cause fractures along the alloy interface when stresses are exerted, with resultant separation along the interface between the iron base and the aluminum coating deposit.

According to the instant invention, an interalloying for an interface thickness of only a few atom diameters is produced. Therewith, controls are provided for the presentation of a completely clean substrate surface, for the temperature at which interdiffusion of substrate and coating is being effected, and for the time duration for which

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the coated material is subjected to a temperature at which the alloying will occur.

It has previously been proposed to clean the surface of a ferrous sheet in various ways. For example, in galvanizing, a steel strip is heated in air or oxygen to burn off oils, and then it is heated at 900 to 1,200 degrees F. in hydrogen to reduce surface oxides back to elemental iron. Therewith, the reducing chamber contains hydrogen at super-atmospheric pressure, and the sheet is advanced to a zinc-coating bath, noting that the hydrogen is not then of great harm to the plating but may assist in keeping the bath low in zinc oxide. When this procedure of cleaning is employed on ferrous sheets which are then to be subjected to vacuum deposition, however, at least two seals must be present to guard the hydrogen-reduction chamber; one to prevent loss of the hydrogen to the atmosphere, and another which is effective at a greater pressure differential to separate the super-atmospheric hydrogen chamber from the vacuum deposition chamber.

According to this invention, a hydrogen removal of surface oxygen is effected by storing hydrogen within the body of the substrate, and later withdrawing this hydrogen through the surface under a temperature condition at which the hydrogen is effective to reduce surface oxides: and includes the employment of this hydrogen-withdrawing step as a means of also ridding the substrate of chemisorbed oxygen, air-adsorbed oxides, carbonates, hydroxides, and other volatile or evaporable impurities.

An object of the invention is the employment of a surface cleaning operation for the purpose of introducing and storing hydrogen within the metal substrate, followed by a preliminary evacuation for withdrawing the hydrogen through the surface of the substrate, with a heating during the withdrawal, and then by a deposition of metal upon the substrate.

Another object of the invention is the surface cleaning of a metal substrate with storage of hydrogen in the substrate stoichiometrically capable of removing surface oxygen present as the substrate is advanced to a first evacuation zone.

A further object is the provision of a metal substrate for vacuum treatment, in which contained hydrogen is present for effecting the elimination of surface oxide wherewith the evacuation also eliminates other gases and vapors, and the cleaned substrate can be advanced to a region at which metal vapor is deposited upon the cleaned surface.

A further object is a procedure in which a primary atmospheric cleaning accomplishes the storage of hydrogen within the substrate, followed by subjection of the heated substrate to evacuation whereby to withdraw the hydrogen and effect thereby a removal of surface oxygen, and followed in turn by the vacuum deposition of metal vapor upon the cleaned surface for a time and temperature period during which alloy formation is restricted.

A further object is a process of preparing a metal-coated metal sheet by cleaning the surface of the metal sheet and storing hydrogen in the body of the sheet, with a subsequent heating and evacuation to cause the stored hydrogen to evolve and be effective for a surface preapration of the sheet, and with a final vacuum deposition of metal thereon at a temperature of insignificant diffusion effects between the metals.

With these and other objects in view, as will appear in the course of the following description and claims, an illustrative embodiment is shown on the accompanying drawing which shows the successive steps in conventionalized form.

In the drawings:

FIGURE 1 shows, in an upright section of conventionalized apparatus, the successive stages of preliminary treatment in one embodiment of the invention;

FIGURE 2 shows an upright section through the reduction and coating parts of a treatment apparatus.

In the drawing a steel strip *S* is unwound from a coil *C* and passed through a first cleaning tank 10 which illustratively contains a solution 11 of an alkali such as alkaline orthosilicate or alkaline phosphate, with an inhibitor and a wetting agent, such as that prepared with the product known in commerce by the trademark "Orthosil." A desirable concentration is 4 ounces per gallon at 170 to 190 degrees F. The strip *S* is preferably subjected to electrolysis in the bath solution 11, e.g., as the cathode between plates 12, with current from the generator 13 by conductors 14. The strip *S* is then passed through a scrubbing tank 16 having the illustrative brushes 17 for removing loose surface films before passing into the tank; and then rinsed, e.g., by water from nozzles 15 to remove residues.

Rollers 18 are employed to guide the strip *S* to and through the successive cleaning regions.

From the scrubbing tank 16, the strip *S* is preferably passed into a tank 20 containing an acid bath 21. This bath illustratively is a warm 4 percent solution of sulfuric acid, containing about 1/2 percent of yellow phosphorus mixed therein. The tank 20 has the plates 22 connected by conductors 23 to a generator 24, so that the steel strip is cathodic. A low-voltage, low-amperage current of about 1/2 ampere per square inch of strip surface is employed. A desirable temperature is 150 degrees F.

In practice, low carbon steel may have a content of 0.05 to 0.10 part per million of hydrogen, dependent upon its history. The above cathodic charging in acid bath can store up to about 3 parts per million therein. When the yellow phosphorus is present in the acid bath, the cathodic charging can effect storage of up to 14 parts per million. The expression of "parts per million" refers to parts by weight; that is, one part per million means that 0.0001 percent by weight of hydrogen is present in the ferrous material. This hydrogen storage occurs within the atomic lattice structure of the ferrous body. The accepted value of solubility of hydrogen in the ferrous metal is less than 0.01 part per million at room temperature. Cathodic treatment in alkaline bath releases most of the developed hydrogen into the bath in molecular form so it escapes as bubbles but with a small amount being absorbed into the steel. With the instant acid bath with phosphorus, a large part of the hydrogen enters the metal body in a nascent form.

The procedure is likewise applicable to other substrate materials. In general, it is applicable to carbon and alloy steels which are basically of ferritic structure, i.e., in which the matrix crystals are of body-centered cubic form and are predominantly iron, that is, over 50 percent thereof. The time of residence in the hydrogen-storing step depends upon the substrate composition, noting that full storage to maximum content throughout the body is not required.

The time required for provision in the metal body of an amount of hydrogen adequate for the removal of surface oxygen is correlated to the exposure of the sheet after the storage therein. In general, the previous cleaning steps have removed surface impurities, and the cathodic treatment provides a surface essentially free of oxides and oxygen. If the cathodically treated strip *S* passes from the tank 21 and enters the seal 30 shortly thereafter, the intervening rinsing and drying produce no visually perceptible coating of oxygen-containing matter; and correspondingly one p.p.m. of hydrogen can be sufficient for the later removal. Therewith, a continuous movement of the strip with a few seconds of cathodizing residence in tank 21, and a few seconds exposure to rinsing water and air prior to entry into seal 30, is effective. Under such continuous line conditions, a saturation with hydrogen for the outer parts of the strip can be sufficient, and the diffusion time allowance can be short. When longer exposures to water and air are employed, a longer

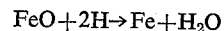
residence in the cathodizing vat 21 is required: for example, a saturation to 14 p.p.m. of a steel strip 0.009 inch thick may require 15 to 30 minutes, depending upon the diffusion rate at the strip temperature, e.g., 150 degrees F.

From the tank 20, the strip *S* passes through a hot water rinse tank 35 and between the nozzles 26 by which hot air is blown upon the strip to dry the same.

The cleaning operations in tanks 10, 16, 20, 25 are performed at atmospheric pressure; and the tanks can be open to the atmosphere.

After drying, the strip *S* is passed through a succession of chambers shown in section in FIGURE 2. Therewith, the strip passes a first or inlet seal 30 into an antechamber 31 which is evacuated through the pump connection 32, and thence through a second or intermediate seal 33 with an evacuation connection 33a into the reduction chamber 34 having an evacuation pump connection 35. The pressure in chamber 34 is at about 0.020 mm. of mercury (20 microns); and that in the antechamber 31 at some higher pressure lower than atmosphere. At such pressures, the hydrogen stored in the strip *S* will escape slowly at room temperature: after 72 hours in such cool chambers, hydrogen still remains.

The strip *S* is heated in the chamber 34, illustratively by the induction coils 36 supplied with high frequency current from the conventionalized supplies 37. The strip is thereby heated to 300 to 1,000 degrees F., wherewith the rate of hydrogen withdrawal is increased, e.g., up to about one hundred times. Therewith, the solubility factor of hydrogen in steel is also increased, but remains below one part per million at 1,000 degrees F. compared to 10, 12 or more parts per million stored in the ferrous base. The hydrogen therefore is withdrawn at the surface of the strip, and diffuses from the interior of the strip body rapidly and in proportion as the surface layers are stripped of excess hydrogen. This hydrogen is released at the surface largely in atomic or nascent form, and is highly reactive as compared to the prior employments of super-atmospheric pressures of molecular hydrogen around the ferrous base. As the atomic hydrogen passes any superficial surface oxygen in chemisorbed, oxide, or other form, it displaces the oxygen therefrom and water vapor is formed and carried from the surface by subsequent hydrogen atoms. When a unit area of the surface has been cleaned, subsequent hydrogen atoms passing outward through this surface area shortly thereafter unite to form molecular hydrogen. In practice, oxygen present at the surface is usually a thin layer in chemisorbed condition with the instant procedure, and hence partakes rapidly in a reaction



The continued evolution of the stored hydrogen and removal of water vapor are effective to drive the reaction toward the right in this equation, as a matter of chemical mass action, noting that the water vapor is being constantly removed by the evacuation and by the effect of the evolving hydrogen.

In practice, the pressure in the removal chamber 34 is held at 20 to 50 microns, with the evacuation connection 35 removing water vapor and hydrogen. As brought out below, the reaction proceeds at temperatures of 300 degrees F. and above: a practical maximum is about 1,000 degrees F. Preferably, the rate of travel and time of vacuum/heating exposure is such that the stored hydrogen is reduced to 2 or 3 parts per million or below. Such pressures in chamber 34 are more economical than maintenance of pressures of 1 micron or below which are requisite for good vacuum metallizing of the cleaned strip.

In practice, a time:temperature relation must be observed, based on a rate constant t_0 defined as

$$t_0 = t A e^{-Q/RT}$$

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where A is a parameter determined by the diffusing atom present, e.g., hydrogen; t is time; T is temperature; Q is the activation energy for diffusion of the hydrogen; and R is the gas constant. When an optimum time t_1 has been found for temperature T_1 , the time t_2 for another temperature T_2 can be roughly computed as

$$T_2 = \frac{1}{(R/Q) (\log t_2/t_1) 1/T_1}$$

The time of treatment is a function of the speed of movement through the chamber 34 and the length of path in this chamber. The temperature is determined by heating effects of the coils 36.

In practice, the strip S can move at speed rates of 10 to 1,000 feet per minute, and the temperature during the reduction can be kept in the range of 300 to 1,000 degrees F.

From the chamber 34, the strip passes through a third or deposition chamber seal 40 into the vacuum deposition chamber 41 having vaporizer elements 42 which are resistively heated by current from the bus bars 43, 44. The coating metal can be supplied to the heated elements 42 as wires 45 which are melted and the molten metal evaporated at the low pressure, so that its vapor deposits on the strip S. The chamber 41 is evacuated by a connection 46 to a group of diffusion, booster and back-up pumps as known in the art, so that a vacuum coating pressure below one micron is maintained.

For minimum alloying of the deposited aluminum coating metal with the metal of the substrate, the substrate should be at a temperature below about 600 degrees F., at which the rate of interdiffusion is very low. Successful deposits have been obtained at room temperature. At temperatures approaching 1,000 degrees F., the counter-diffusion of aluminum and iron, for example, into one another at the coating interface is so rapid that complete alloying may occur in a very short time. The strip can be cooled in various ways. When the strip speed is high, and a high temperature is being employed in the removal chamber 34, and the distance of travel from the removal chamber 34 to the coating region in the deposition chamber 41 is short, positive cooling devices 47 such as water-cooled hollow plates may be employed, and the exit guiding and sealing rolls 38 may also be water-cooled for contact cooling. When the strip speed is low, and a relatively low temperature is being employed in the removal chamber 34, and the distance of travel from the removal chamber 34 to the coating region is adequate, the cooling may be produced by radiation losses.

From the seal 40, the strip enters the chamber 41 at a temperature lower than that in the chamber 34, by radiation cooling in passing the seal 40 and assisted by having the guide rolls 38 at the outlet slit from the seal 40 water-cooled, with feasibility of employing water-cooled devices 47 at the inlet to the chamber 41 when the strip is moving rapidly with a high temperature in chamber 34 and the vacuum deposition is to be performed at a low temperature. The strip is turned downward by a roll 48, passes through the vapor deposition region between the vapor generating elements 42, and moves around a lower guide roll 49, enters the outlet seal 50 having the evacuation ducts 51a and the rollers 51, and thence moves to a driven take-up reel 55 in the atmosphere. Therewith, the thickness of the intermediate alloy bonding layer is controlled by the rate of strip feeding, the distance of strip movement while hot and with the coating metal thereon, and the temperature of the strip during the depositing and bonding.

The several seals are illustrated as having rolls 38, 51 which engage opposite faces of the strip S, the rolls fitting at their ends against the side walls of the structures and having the flexible blades 60 in contact with their surfaces to restrict leakage around the rolls. The rolls are located between pairs of walls 61 which are positioned adjacent the rolls and have slits through which the strip moves.

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The temperature of the substrate during vacuum deposition can be from room temperature or below, up to about 600 degrees F. with aluminum, with preference for the lower temperatures; and the temperature at deposition should always be below the temperature employed for the prior oxide reduction and oxygen removal. For example, with the removal being performed at 300 degrees F., the coating can be at room temperature: with removal at 900 degrees F., which permits a rapid movement of the strip, the coating can be at temperatures up to 600 degrees F., noting the short time of residence at the coating region and the quick cooling which can be effected thereafter to minimize alloying. By thus having the substrate temperature higher during the gas removal phase, diffusion is promoted: and by having a lower temperature during vacuum deposition not only is alloying restricted, but also the escape of further hydrogen is restricted. One optimum relationship is that at which the hydrogen evolution during the removal at the higher temperature causes the hydrogen level at the surface to be coated to be at equilibrium in the metal at or above the vacuum coating temperature.

The conditions for oxygen removal by the issuing hydrogen involve a time: temperature factor, with a longer time, e.g., of minutes, being required at, say, 300 degrees F., while less than a minute is required at, say, 600 degrees F., and as low as a fraction of a second at 1,000 degrees F. Thus, a rapid rate of substrate travel is feasible at the latter temperature range. Likewise, the diffusion of hydrogen provoked by the increased temperature, and its evolution from the substrate metal upon evacuation, renders possible the removal treatment with lower amounts of hydrogen stored therein, e.g., 2 or 3 parts per million, when the charged strip passes quickly from the bath through a drying zone and into the removal region without significant contact with the air.

In the preparation of sheets of CMQ black plate, 0.009 inch thick, having the normal thin layer of cotton-seed oil on the bright surface, and effecting deposits of aluminum at about 40 millionths of an inch, with cooling in vacuum, the coating was bright and had high reflective ability. If withdrawn at a temperature of 300 degrees F. or over, the surface had a milky white appearance. Tests for adhesion under differing conditions of treatment were made by a so-called Olsen test, with the formation of a spherical indentation about one inch in diameter and 0.3 inch deep: with non-adherent coatings, the surface deposit flaked off, while with adherent coatings there was no separation even at the edge of the cup-fractures.

For comparable test purposes, small sheets were cleaned in various manners, rinsed in hot water, dried by a warm air blast, placed in a Kinney vacuum coater, and evacuated to a pressure of 0.04 to 0.09 micron, which is a better vacuum than employed in commercial vacuum metallizing units. An electrical resistance heater was applied at one side of the sheet, for bringing the sheet to a specified coating temperature: the sheet was held at this temperature for from about 15 seconds to five minutes, and then aluminum vapor was generated and delivered to the sheet for deposition thereon.

It was found that sheets cleaned with solvent degreasing agents, with abrasive grinding, wire brushing and like mechanical operations, placed in the vacuum chamber, evacuated and coated cold, showed no adhesion of the coating. Sheets cleaned electrolytically in a 5 percent solution of the aforesaid Orthosil at 160 degrees F. with the sheet as cathode, at a potential drop of 6 to 12 volts to maintain a current density of 2 amperes per square inch for 45 seconds; with cold evacuation and cold deposit as before, gave no adhesion of the coating.

Sheets electrolytically cleaned in the Orthosil solution as before, then heated in vacuum at 300 to 500 degrees F. and coated while at such temperature, showed differing adhesion effects. At the lower part of the temperature

range, adhesion was uncertain and hence unsatisfactory: at the upper part and with long heating of the coated sheet, the brittle alloy caused delamination of the coating. Coatings at 375 degrees and over showed excellent static adhesion: the sheets prepared at 375 and 400 degrees F. showed excellent mechanical properties with no detectable thickness of alloy layer.

Sheets electrolytically cleaned in the Orthosil solution as before, then cathodically charged with hydrogen in a sulfuric acid electrolyte, and heated in vacuum at 300 degrees F. for 30 minutes, cooled, and coated cold, showed excellent adhesion; indicating that the effect of the heating and evacuation before coating produced a receptive surface condition without need for a diffusion heating and therewith avoiding the possibility of an excessive alloy layer by exposure at the diffusion temperature.

Sheets electrolytically cleaned in Orthosil as before, washed and evacuated quickly before any significant oxide could form, heated in vacuum to 400 degrees F. for 30 minutes, cooled to room temperature, and vacuum coated cold, showed excellent adhesion. This likewise indicates that a pretreatment, with sufficient stored hydrogen to complete the cleaning and preparation of a purely metallic surface, is effective.

Sheets electrolytically cleaned in Orthosil as before, washed, cathodically charged with hydrogen in the aforesaid acid bath, rinsed, evacuated cold and coated cold, showed various effects. Often the coating peeled: in a few cases there was adhesion. This establishes that, for repeatable results, the primary evacuation with hydrogen evolution should be at a temperature of about 300 degrees or over, to assure the removal of surface oxygen.

It has been found that heating to 600 degrees F. for a few seconds in vacuum is adequate to prepare a freshly cathodized surface so that excellent adhesion is later attained with vacuum deposition upon the sheet whether hot or cold.

The employment of the acid cathodizing bath 21, the composition of this bath, and the extent of treatment therein are determined by the base metal and thickness of the sheet, the behavior of the deposit metal thereon, the temperature of the vacuum treatments, and the length of time between the emergence of the strip from the bath 21 and its entry into the vacuum deposition apparatus. For example, when the strip is dried, cooled and stored for a time before being delivered into the vacuum deposition apparatus, full advantage should be taken of the ability to store 12 or more parts per million of hydrogen: whereas when the strip is to be coated at once, the cathodic acid bath may be dispensed with, and the strip passed directly from the scrubbing bath 17 to the hot blast nozzles 26 and into the coating apparatus. In the latter case, the heaters 36 are adjusted to give a sheet temperature of say 600 degrees F., and the strip is then cooled so that it receives its coating in chamber 41 substantially at room temperature. The temperature for the strip S in the removal chamber 34 and the evacuation thereof can be selected for optimum employment of the hydrogen stored therein and for the removal of this hydrogen, and the water vapor formed thereby in reducing oxygen, so that the strip S is clean and free of gas- ing while in the vacuum deposition zone opposite the elements 42. Therewith, the strip temperature during reduction can be from 600 to 1,000 degrees F. and above.

The procedure is applicable with metal substrates having a body-centered cubic habit, for facilitating the bonding of later-applied metal coatings thereto: for examples, bodies of carbon irons and steels and alloyed irons and steels having a major matrix component of ferritic structure, including molybdenum and chromium steels. Likewise, the substrate need not be a sheet or web of such metal because separate articles, e.g., casting of the metal, can be cathodically treated to store hydrogen therein, and then heated in vacuum for effecting the removal of surface

oxygen-containing films by batch or conveyor operations. Further, coatings other than aluminum, including titanium, chromium and cadmium, may be vacuum deposited upon such substrates cleaned by this procedure, to attain adherent coatings. When the coating metal does not form a brittle or otherwise deleterious alloy at the interface, the temperature:time restrictions stated for aluminum need not be observed: for example, tenacious titanium coatings, upon CMQ black plate which has been cleaned by the procedure, can be deposited in the temperature range of 515 to 860 degrees C., with the product having a coating thickness of about 12 to 18 millionths of an inch and exhibiting no traces of oxide or nitride by X-ray diffraction tests. The coatings can be effected by procedures other than vacuum deposition: e.g., steel sheets may be passed from the removal chamber into a further chamber containing molten tin or zinc, with care to exclude oxidizing agents from contact, and deposition from carbonyls and other metal-releasing atmospheres may be utilized.

The term "CMQ black plate" is used herein to define the can making quality black plate referred to in Steel Products Manual, Section 14, of American Iron & Steel Institute, August 1949, and is a commonly used abbreviation in that art.

The term "chemisorbed" is used herein as referring to chemical adsorption; noting "The Encyclopedia of Chemistry," by Clark-Hawley (Reinhold, 1957), page 20. Physical adsorption is there noted as presumably occurring by Van der Waals forces; whereas "chemical adsorption (chemisorption) differs from physical adsorption in that it depends upon chemical bond formation between the adsorbent and the adsorbate."

The illustrative embodiments are not restrictive, and the invention may be practiced in many ways within the scope of the appended claims.

What is claimed is:

1. The method of preparing a metallic coated article from a body having a surface presented by a ferrous metal having a major matrix component of ferritic crystalline molecular structure and having a reducible oxygen-containing film on said surface, which comprises cleaning the surface of the body by an alkaline solution and thereafter as cathode in an acid solution whereby hydrogen atoms are stored within the atomic lattice structure of the said surface metal in quantity in excess of that required for reducing the surface oxygen thereon, rinsing the surface and drying the same, then subjecting the body to evacuation while heating to a temperature of 300 to 1000 degrees F. for effecting withdrawal of hydrogen therefrom in atomic form and reduction of the said oxygen-containing film by the evolved hydrogen, cooling the body to a temperature below that of the hydrogen withdrawal and below 600 degrees F. whereby further withdrawal of hydrogen is restricted, preventing access of oxidizing agents to said body, and thereafter with maintained exclusion of oxidizing agents exposing the said surface during evacuation at the lower temperature to the vapor of a metal selected from the group consisting of aluminum, titanium, chromium and cadmium and effecting deposition of the metal vapor as an adherent coating on said body.

2. The process of claim 1, in which the evacuation for withdrawal of hydrogen is at 20 to 50 microns, and the evacuation for deposition of the metal vapor is at not over 1 micron.

3. The process of claim 1, in which the exclusion of oxidizing agent is attained by maintaining a vacuum around the body between the step of hydrogen withdrawal and the step of metal deposition.

4. The process of claim 1, in which the body is a ferrous sheet, and the metal vapor is aluminum, and in which the hydrogen withdrawal is at 300 to 600 degrees F., and the metal deposition is at about room temperature.

5. The method of preparing a metallic coated article

from a body having a surface presented by a ferrous metal having a major matrix component of ferritic crystalline molecular structure and having a reducible oxygen-containing film on said surface, which comprises cleaning the surface of the body by an alkaline solution and thereafter as cathode in an acid solution whereby hydrogen atoms are stored within the atomic lattice structure of the said surface metal in quantity in excess of that required for reducing the surface oxygen thereon, rinsing the surface and drying the same, then subjecting the body to evacuation while heating to a temperature of 300 to 1000 degrees F. for effecting withdrawal of hydrogen therefrom in atomic form through the said film and reduction of the said oxygen-containing film by the evolved hydrogen and essentially until the residual amount of hydrogen in the body is that of equilibrium in the metal at the predetermined coating temperature, cooling the body to a coating temperature below that of the hydrogen withdrawal and below 600 degrees F., preventing access of oxidizing agents to said body, and thereafter with maintained exclusion of oxidizing agents exposing the said

surface during evacuation at a temperature below that of the hydrogen withdrawal to the vapor of a metal selected from the group consisting of aluminum, titanium, chromium and cadmium and effecting deposition of the metal vapor as an adherent coating on said body.

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