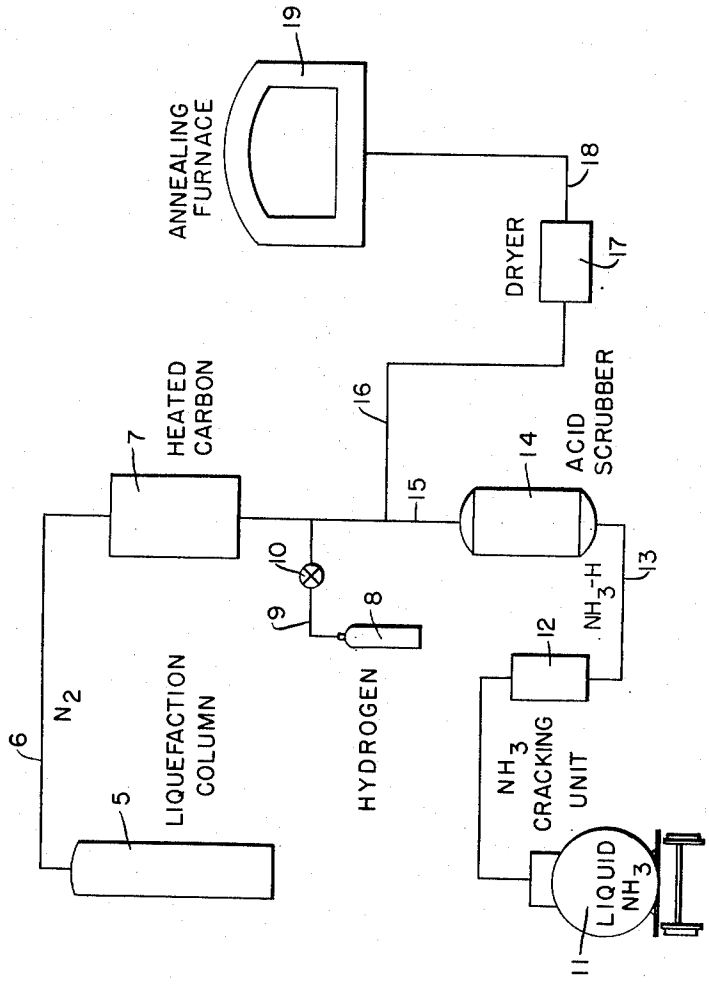
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METHOD OF PREPARING SURFACES FOR TINNING

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METHOD OF PREPARING SURFACES FOR TINNING

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This invention relates to the coating of ferrous metals, particularly cold rolled steel strip, with tin, either by hot dipping or by the electrolytic process, and to the preparation of the surface of the metal to receive the tin coating.

Annealing of the cold rolled steel is a necessary initial step in the production of tin plate. This is accomplished by heating the strip, usually in the form of coils, to relatively high temperatures. In order to prevent oxidation of the metal, it has been customary to provide an inert, oxygen-free atmosphere in the annealing furnace.

Such an atmosphere does not, however, ensure the production of a surface condition on the strip which will afford the best bonding of the tin thereto. The surface invariably contains iron carbide which is not affected by the inert atmosphere heretofore used in annealing. The iron carbide in the surface of the metal is detrimental to bonding of tin to the metal.

It is the object of the present invention to provide a method of coating tinplate stock with tin, and particularly a method of coating tinplate stock with tin in which the tinplate stock is bright annealed in a non-oxidizing, decarburizing atmosphere which will reduce the iron carbide on the surface of the stock to substantially pure ferrite to which tin will readily bond.

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specification and the accompanying drawing, which illustrates diagrammatically an apparatus suitable for the practice of the method.

I have discovered that the surface of ferrous metals such as cold rolled steel strip can be modified to eliminate iron carbide therefrom and to provide thereon a thin surface layer of ferrite to a depth of from 0.0005 to 0.030. This is accomplished by subjecting the metal at annealing temperatures in the neighborhood of 1200° F. to an atmosphere of nitrogen-containing hydrogen or carbon dioxide or both, provided that the atmosphere is free from oxygen and water vapor. The presence of small amounts of carbon monoxide which is generally incident to the inclusion of carbon dioxide under the conditions of operation is not detrimental. The invention depends primarily upon the provision of an inert gas such as nitrogen, modified by the addition of hydrogen or carbon dioxide or both. Hydrogen and carbon dioxide react with iron carbide above annealing temperature to produce ferrite on the surface according to the reactions

$$Fe_3C + 2H_2 \rightleftarrows 3Fe + CH_4$$

and

$$Fe_3C + CO_2 \rightleftarrows 2CO + 3Fe$$

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In carrying out the reaction, I prefer to employ nitrogen produced in the separation of the atmosphere by liquefaction and rectification. Such nitrogen is readily available and is free from water vapor but contains usually upward to 3% of oxygen. The oxygen may be removed by passing the nitrogen through a bed of heated carbon such as charcoal. Such treatment produces carbon dioxide and carbon monoxide in small proportions. If the bed of heated carbon is at a sufficiently low temperature the ratio of carbon monoxide to carbon dioxide will be so low that the resultant gas will be sufficiently decarburizing, even though it may contain some carbon monoxide. Consequently, the presence of small amounts of carbon monoxide in the annealing atmosphere is not detrimental, though not essential to the practice of the invention. The carbon dioxide is actually desirable for the purpose of eliminating iron carbide from the surface of the metal.

Hydrogen may be supplied from any suitable source as, for example, hydrogen compressed in cylinders or produced by decomposition of ammonia, and can be added to the nitrogen in proper proportions before the gaseous mixture is delivered to the annealing furnace.

The preferred proportions of the gases in the mixture are as follows:

Nitrogen	Hydrogen	Carbon Dioxide
Percent	*Percent*	*Percent*
95 to 99	1 to 5	----------
95 to 99	----------	.1 to 1
95 to 99	.1 to 1	.1 to 1

As indicated, carbon monoxide may be present in small proportions, preferably not over 5%, but it is not essential or detrimental to the desired reaction.

While we prefer to use nitrogen obtained as a by-product in the production of oxygen from the atmosphere, nitrogen from any other sources may be used also. If no oxygen is present in the nitrogen, it is not necessary to pass it through heated carbon to eliminate the oxygen. In that case, carbon dioxide may be omitted or it may be added from any suitable source.

The procedure as described effects an intense decarburization of the surface of the metal and the formation of a thin layer of ferrite thereon. This has been found to produce a markedly superior bond with tin when the latter is applied by hot dipping and especially if the tin is applied by the electrolytic process. It is unnecessary to subject the metal to pickling after annealing, as in the usual practice. The avoidance of this step reduces the cost and also ensures an im-

proved coat of metal which is more resistant to corrosion because of the increased adherence of the tin to the ferrite on the surface of the metal.

Referring to the drawing, 5 indicates a liquefaction column in which atmospheric air is separated and from which nitrogen is withdrawn through a pipe 6. Since the nitrogen in the liquefaction column usually includes small amounts of oxygen, the gas is delivered through the pipe 6 to a chamber 7 in which it is subjected to the action of heated carbon. The oxygen is consumed in oxidizing the carbon, producing carbon dioxide and some carbon monoxide. Hydrogen may be added in the required proportions from a cylinder 8 through a pipe 9 controlled by a valve 10. Preferably liquid ammonia is stored in the container 11 and delivered to an ammonia cracking unit 12 where heat is supplied in sufficient amount to break down the ammonia into its components, nitrogen and hydrogen. These are delivered through a pipe 13 to an acid scrubber 14 for the purpose of neutralizing any ammonia which may remain in the gases. The mixture of nitrogen and hydrogen is delivered through a pipe 15 to the pipe 16 carrying the nitrogen and carbon dioxide from the chamber 7. The mixed gases may be delivered to a drying unit 17 of any suitable type in the event that any moisture remains therein, so that all the water vapor is removed. Thereafter the gaseous mixture is delivered through a pipe 18 to the annealing furnace 19 in which the material to be treated is subjected to an annealing temperature in an atmosphere consisting of the gaseous mixture supplied thereto. The annealing operation may be continued for varying periods, depending upon the nature of the material treated and the desired modification of the surface. Usually heating to a temperature of approximately 1200° F. over a period of 8 hours is sufficient to accomplish the desired purpose, that is, the formation on the surface of a thin layer of ferrite. After cooling in an atmosphere of the treating gas, to eliminate the possibility of oxidation, the treated material may be removed and will be found to be in condition for the application of a coating of tin without pickling or other further treatment.

Material savings are accomplished by the procedure as described. Furthermore, the sheets, prepared in accordance with the invention and coated with tin, display superior resistance to corrosion in use. The coated sheets are particularly desirable for the production of cans in which the tin coating may be subjected to the acid constituents of fruits and vegetables stored in the cans.

Various changes may be made in the form and arrangement of the apparatus used and in the details of the procedure without departing from the invention or sacrificing the advantages thereof.

I claim:

1. The method of converting iron carbide at the surface of ferrous tinplate stock to ferrite preparatory to coating said stock with tin which comprises maintaining the surface of the stock having the iron carbide thereat, while at an annealing temperature, in intimate contact with a non-oxidizing, decarburizing gaseous atmosphere containing from 95% to 99% nitrogen and 0.1% to 5% hydrogen until the iron carbide is reduced to ferrite.

2. The method of converting iron carbide at the surface of ferrous tinplate stock to ferrite preparatory to coating said stock with tin which comprises maintaining the surface of the stock having the iron carbide thereat, while at an annealing temperature, in intimate contact with a non-oxidizing, decarburizing gaseous atmosphere containing from 95% to 99% nitrogen, 0.1% to 1% hydrogen and from 0.1% to 1% carbon dioxide until the iron carbide is reduced to ferrite.

3. The method of converting iron carbide at the surface of ferrous tinplate stock to ferrite preparatory to coating said stock with tin which comprises maintaining the surface of the stock having the iron carbide thereat, while at an annealing temperature, in intimate contact with a non-oxidizing, decarburizing gaseous atmosphere containing from 95% to 99% nitrogen and from 0.1% to 1% carbon dioxide until the iron carbide is reduced to ferrite.

4. The method of converting iron carbide at the surface of ferrous tinplate stock to ferrite preparatory to coating said stock with tin which comprises maintaining the surface of the stock having the iron carbide thereat, while at a temperature of approximately 1200° F., in intimate contact with a non-oxidizing, decarburizing gaseous atmosphere containing from 95% to 99% nitrogen and from 0.1% to 5% hydrogen until the iron carbide is reduced to ferrite.

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