METHOD FOR COATING STEEL WITH NICKEL

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11 Claims. (Cl. 29—420.5)

The present invention is directed to a special method for producing nickel coatings on steel and, more particularly, to a special method for producing nickel coatings of good quality on flat steel products using nickel powder as the source of nickel.

Steel strip coated with a thin nickel layer to give an attractive corrosion-resistant finish is usually produced by well known electroplating techniques or by rolling a composite billet in which a thin nickel strip is welded to the basic steel. Such prior methods have been attended by relatively high cost with the result that they have only been employed in special situations in which the cost thereof could be tolerated. A demand has existed in the art for a method which would provide nickel coatings of high quality on flat steel products at high rates of production and at a cost which would enable the material to compete with other known procedures for applying corrosion resistant coatings to steel. We have now provided a method for achieving the foregoing objectives.

It is an object of the present invention to provide a method for achieving nickel coatings of good quality on flat steel products at high rates of production and at a low cost.

It is another object of the invention to provide a method for coating relatively large steel surfaces with a nickel coating of good quality.

It is still another object of the invention to provide a method for providing flat steel products with a corrosion resistant coating having good surface appearance.

Other object and advantages of the invention will become apparent from the following description:

We have now found that corrosion resistant coatings can be applied to steel strip by using an aqueous slurry of particulate nickel which is spread onto the steel. The coated strip is heated to sinter the coating and subsequently the coating is densified by rolling and, if necessary, further sintering. By this means, a substantially impermeable layer of nickel having negligible porosity and a good surface finish can be obtained.

Broadly stated, the present invention is directed to a method for producing a corrosion resistant nickel coating on steel which comprises coating surfaces of flat steel products with an aqueous slurry containing about 45% to about 80% by weight of fine nickel powder having a particle size of about 2 microns to about 10 microns together with up to about 10% by volume of inert particles having a particle size of about 0.01 to about 50 microns and up to about 0.1% to 0.5% by weight of an organic binder, drying the resulting slurry coating, sintering the dried coating in an atmosphere protective to steel at a temperature of about 700° C. for 60 minutes to about 1200° C. for 10 seconds, and compacting the sintered coating as by rolling so as to provide a consolidated nickel coating on the steel.

Advantageously, the slurry is applied to the steel in amounts equivalent to twice to four times the desired final thickness.

Advantageously, the organic binder employed is methyl cellulose as this material can readily be volatilized by heating the slurry coating. For best results, a nickel powder having a particle size of about 3 to about 7 microns is employed. When inert particles are employed in the slurry so as to provide a final nickel coating which yields a micro-cracked or micro-porous chromium coating upon chromium plating, it is advantageous to employ at least up to about 10% of inert coated powder, by volume of slurry. The steel surface may be prepared to remove oxides therefrom prior to slurry coating but in some cases the steel surface may, in fact, be oxidized. It is essential to degrease. If the strip has been hot rolled, it is important to remove the thick oxide layer.

In an advantageous embodiment of the invention, the prepared steel surface is coated with a copper layer which is at least about 3 microns thick.

It is found to be of considerable importance for the satisfactory preparation of a corrosion resistant layer of nickel by the use of an aqueous slurry that the slurry is so formed that it produces a homogeneous mixture which is smooth in appearance. This may be achieved in practice by high-speed mixing and by the use of surfactants to remove any foam which is formed. We find that the smoothness of the slurry should be such that it offers to the eye an appearance of a creamy consistency.

One method of preparing the slurry is to mix an organic binder with a quantity of boiling water to which may then be added an equal quantity of cold water. To this warm solution, which is continuously agitated, is added a surfactant to remove any foam which may form. To the solution is now added a quantity of nickel powder, for example, the type prepared by the thermal decomposition of nickel carbonyl, and this is thoroughly mixed in to give a slurry having a creamy consistency. The slurry is spread onto the steel strip and while the slurry is still wet the strip may be vibrated to encourage close packing of the particles. An electromechanical vibrator adapted to apply vibrating impulses at a frequency of about 50 cycles per second or higher to the strip carrying the slurry coating may advantageously be employed.

In a second method, the aqueous slurry may be applied by means of a conventional spray gun as used for paints. This method has the advantage over the former method in that it is not necessary to have a perfectly flat surface on which to apply the slurry and, hence, the method can be applied to strip of much greater width than that to which the spreading technique can be used. The resistance to corrosion of coatings prepared in this way is equally as good, if not better, than that of coatings prepared by the spreading technique.

In a further method, the slurry may be applied by the "curtain-coating" technique in which the slurry is forced through a narrow slot to form a continuous vertical curtain through which the steel strip is passed. For this purpose, it is preferable to employ a thicker slurry than that used in the other methods described hereinafter.

Another method is to apply the slurry by "reverse roller coating" technique and, in fact, many of the methods used in industry for the application of viscous coatings can be utilized.

The strip and the slurry are conveniently dried at low temperature and subsequently sintered in a reducing atmosphere. The strip carrying the sintered nickel layer is then rolled to densify the nickel, may be resintered and cold rolled to augment the densification and to give the nickel layer a high surface finish. A final annealing step is highly desirable especially when the strip is to be fabricated. It is advantageous first to sinter and then to effect densification since an initial polishing of the coated strip followed by the sintering may produce nonuniform shrinkage effects which cause localized areas of high porosity.

Further improvement in corrosion resistance of the strip can be obtained by employing a final heat treatment at about 500° C. to about 800° C., e.g., about 700° C., for
about 60 minutes to about 2 minutes, e.g., about 12 minutes.

To produce a nickel layer which is still less porous, according to a further feature of the invention we coat the steel with a layer of copper and then apply the nickel slurry to the copper layer. The copper yields a liquid phase upon sintering which accelerates the process of densification. Alternatively, up to about 10% by weight of copper powder may be included in the nickel slurry and the copper-nickel slurry applied to the steel strip.

In order to give those skilled in the art a better understanding of the invention, the following illustrative examples are given:

Example I

A creamy slurry having the following composition was formed:

Water ————————————ml— 100
Nickel powder—
Bulk density 1.6 to 2.1 g/cc. Particle size 3 to 4 microns (by a Fisher Sub-sieve Sizer) ——— g— 250
Methyl cellulose ———— g— 0.5
“Texafor D5” ethoxylated glyceride oil surfactant
Ethoxylated 5:1 to the base ———— g— 0.5

The slurry was applied to a previously pickled black mild steel strip (0.065 inch thick) and the coating thickness was controlled to approximately 0.008 inch by means of a doctor blade.

The slurry was dried and the coated strip was sintered for two minutes at 1150° C. in a cracked ammonia atmosphere by passing the strip through a furnace with a one foot long hot zone at 6 inches per minute. The strip was cold rolled to compact the nickel, resintered for two minutes at 1150° C. in cracked ammonia and finally cold rolled to 0.028 inch and annealed at 700° C. for 12 minutes. This procedure resulted in a substantially impermeable coating of nickel of 0.022 inch thickness.

A series of samples was prepared by this technique and, without application of a further coat of chromium, was exposed for 72 hours to an acetic acid/salt spray as previously defined. Triplicate samples on which the nickel thickness was 0.0022 inch gave protection ratings of 10, 9 and 9 after this test.

Example III

In a further example, a slurry was prepared having the following composition:

Water ————————————ml— 100
Nickel powder—Bulk density 1.75 to 2.1 g/cc.; particle size 3 to 4 microns (by a Fisher Sub-sieve Sizer) ——— g— 287.5
Methyl cellulose ———— g— 0.75
“Supronic” B75 alkylated polyethylene glycol surfactant ———— ml— 0.5

The slurry was forced through a narrow slot 44.8 centimeters long by 0.6 millimeter wide, thus forming a continuous curtain through which the cold rolled and annealed steel strip (1.75 millimeters thick) was passed at 10 meters per minute. The thickness of coating applied was 0.82 millimeter. The coated strip was dried, sintered, rolled and annealed exactly as in the previous example. The final thickness of the nickel coating was 130 microns and the total thickness of the strip, 0.75 millimeter.

Samples were exposed to a copper chloride/acetic acid/salt spray (A.S.T.M. Specification and Tests for Electro-deposited Metallic Coatings, third edition, 1961, page 63) for 24 hours and a rating of 10 was obtained.

According to a further feature of the invention, we form in the slurry a dispersed phase of inert particles, such as, for example, of thorium or alumina, in a size range of about 0.01 to about 50 microns and in a proportion of up to about 10% by volume of the slurry. The inert phase tends to inhibit the sintering and for this reason the particle size should be in the range specified and preferably towards the upper end of the range. The finished product incorporating the dispersed phase has a nickel layer containing widely dispersed inert particles which are able to produce in a subsequently electrolytically applied chromium coating a multiplicity of discontinuities. In this way, we achieve a micro-porous chromium deposit which acts as a corrosion resistant coating. Alternatively, the inert phase may be confined solely to the surface of the nickel layer, for example, by spraying inert particles onto the nickel surface either before or after the initial sintering stage.

### Table

<table>
<thead>
<tr>
<th>Nickel Thickness, thousandths of inch</th>
<th>Period of vibration, cycles per second</th>
<th>Time of vibration, seconds</th>
<th>Voltage Applied to vibrator, V</th>
<th>Protection rating (acetic acid/salt spray)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>50</td>
<td>60</td>
<td>50</td>
<td>(17)</td>
</tr>
<tr>
<td>0.8</td>
<td>50</td>
<td>60</td>
<td>70</td>
<td>(18)</td>
</tr>
<tr>
<td>0.8</td>
<td>50</td>
<td>60</td>
<td>70</td>
<td>(19)</td>
</tr>
<tr>
<td>0.8</td>
<td>50</td>
<td>100</td>
<td>70</td>
<td>(10)</td>
</tr>
</tbody>
</table>

1 After 10 hr. exposure.
2 After 50 hr. exposure.
3 After 100 hr. exposure.

Example II

An example of the use of vibration and of final heat treatment at 700° C. is given below.
It is to be appreciated that the process of the invention enables strip to be coated on both sides simultaneously by passing the strip through a bath of the slurry and controlling the thickness on the strip, for example, by use of a doctor blade. Alternatively, the slurry may be applied by spreading or by curtain coating, dried, and the strip then reversed by passing round a roller and the opposite side coated by the same means. Both sides may also be coated simultaneously by the spray technique. It will be further appreciated that more than one coating may be applied in accordance with the invention. For example, an inner layer may be of nickel alone and a subsequent layer may be of nickel incorporating an inert dispersed phase.

According to still another feature of the present invention, the slurry is adjusted in composition to produce a coating that is an alloy of nickel with either copper or tin or both. In producing a nickel-copper coating according to the present invention, the copper content of the slurry may indeed be as high as 90% by weight of nickel. The tin, which may replace the copper either wholly or in part, may be present in an amount up to about 10% by weight of the nickel.

The alloy is formed during the sintering process. If the slurry contains from 70% to 90% copper by weight of the nickel, the resultant alloy will be a typical cupro-nickel alloy of high copper content. A particularly suitable copper content is about 30%, the result being to produce an alloy substantially identical with the well known nickel-copper alloy that contains about 68% nickel and about 30% copper. It is well known that this alloy pits at a slower rate than nickel and has advantageous properties for resistance to corrosion. The following Example IV is illustrative of the foregoing:

**Example IV**

A creamy slurry having the following composition was formed:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100</td>
</tr>
<tr>
<td>Nickel powder—Bulk density 1.6 to 2.1 g./cc; particle size 3 to 4 microns (by a Fisher Sub-sieve Sizer)</td>
<td>125</td>
</tr>
<tr>
<td>Copper powder—99.5% purity</td>
<td>90</td>
</tr>
<tr>
<td>Methyl cellulose</td>
<td>10</td>
</tr>
<tr>
<td>&quot;Supronite&quot; B75 alkylated polyethylene glycol surfactant</td>
<td>5</td>
</tr>
</tbody>
</table>

The slurry was applied to a cold rolled and annealed mild steel strip (0.063 inch thick) which was vibrated by a vibrator for two minutes at 50 cycles per second and at the amplitude resulting from the use of an applied voltage of 70 volts to the vibrator. The coating thickness was controlled to approximately 0.017 inch by means of a doctor blade.

The slurry was dried and the coated strip was sintered for two minutes at 1050° C. in a cracked ammonia atmosphere by passing the strip through a furnace with a hot zone one foot long at 6 inches per minute. The strip was cold rolled to compact the nickel, resintered for two minutes at 1950° C. in cracked ammonia and finally cold rolled to 0.025 inch. It was then annealed at 700° C. for 12 minutes. This procedure resulted in a substantially impermeable coating of 0.002 inch thickness. The coating contained about 70% nickel and about 30% copper by weight.

As previously noted, the steel may be first coated with a layer of copper, e.g., electrolytically, before the slurry is applied.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for producing an improved corrosion resistant coating on steel which comprises coating a flat steel product with an aqueous slurry containing in suspension between about 45% to about 50% by weight of fine nickel powder and a small amount up to about 10% by volume of inert particles having a particle size from about 0.01 to about 50 microns, drying the resulting slurry coating, sintering the dried coating, compacting the sintered coating to provide a consolidated coating on the steel and chromium-plating at least a portion of the resulting coated steel to provide thereon a micro-porous chromium coating whereby a coating having an improved resistance to corrosion is obtained.

2. A process for producing an improved corrosion resistant coating on steel which comprises applying to a flat steel product an aqueous slurry containing an organic binder, about 45% to about 50% by weight of fine nickel powder, up to about 10% by volume of inert particles having a particle size from about 0.01 to about 50 microns, vibrating the slurry coating, drying the resulting slurry coating, sintering the dried coating and compacting the sintered coating on the steel to provide a consolidated coating on the steel.

3. The process according to claim 2 wherein the steel is coated with copper prior to application of the slurry.

4. The process according to claim 2 wherein the consolidated coating is heated at about 700° C. for about 12 minutes.

5. The process according to claim 3 wherein the slurry contains nickel powder having a particle size of about 2 to about 10 microns and at least a portion of the nickel-coated steel is chromium plated to provide a micro-porous chromium coating.

6. A process for producing an improved corrosion resistant coating on a flat steel product which comprises applying to at least one surface of such a steel product an aqueous slurry containing an organic binder, a surfactant, at least about 45% by weight of fine nickel powder, at least a small amount up to about 10% by volume of inert particles from the group consisting of alumina and thoria having a particle size of about 0.01 to about 50 microns, drying said slurry coating, sintering the resulting dried coating at a temperature of at least about 700° C., subjecting the sintered coating to at least one annealing operation at least one annealing operation to consolidate said coating and to provide a flat steel product having a protective nickel coating.

7. A process according to claim 6 wherein the prepared steel surface is copper-coated to a copper thickness of at least about 3 microns before application of the aqueous nickel slurry.

8. A process according to claim 6 wherein the nickel-containing slurry is applied by spraying.

9. A process according to claim 6 wherein the nickel-containing slurry is applied by curtain coating.

10. A process according to claim 6 wherein the nickel-containing slurry is applied by roller coating.

11. A process for producing a nickel-coated flat steel product which comprises applying to a prepared surface of such a steel product at least one coating of an aqueous slurry containing an organic binder and at least about 45% by weight of fine nickel powder, spraying the slurry coated surface with an aqueous suspension of inert particles, drying the resulting coating, sintering the dried coating at a temperature of about 700° C. to about 1200° C. for about 60 minutes to about 10 seconds, subjecting the sintered coating to at least one rolling operation and at least one annealing operation to provide a flat steel product having a consolidated nickel coating and chromium-plating at least a portion of said consolidated coating to provide a micro-porous chromium coating thereon.
whereby a flat steel product having a coating characterized by high corrosion resistance is produced.

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5 598,653 2/1948 Great Britain.

John F. Campbell, Primary Examiner.
P. M. Cohen, Assistant Examiner.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,316,625

May 2, 1967

George N. Flint et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the heading to the printed specification, line 9, after "28,724/63" insert --; Complete Specification, May 29, 1964 --; column 5, line 61, for "1950° C." read -- 1050° C. --.

Signed and sealed this 9th day of January 1968.

(S Seal)
Attest:
Edward M. Fletcher, Jr.
Attesting Officer

Edward J. Brenner
Commissioner of Patents
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