March 28, 1967 N. M. PARIKH ETAL 3,310,870

PROCESS FOR PRODUCING NICKEL-COATED STEEL

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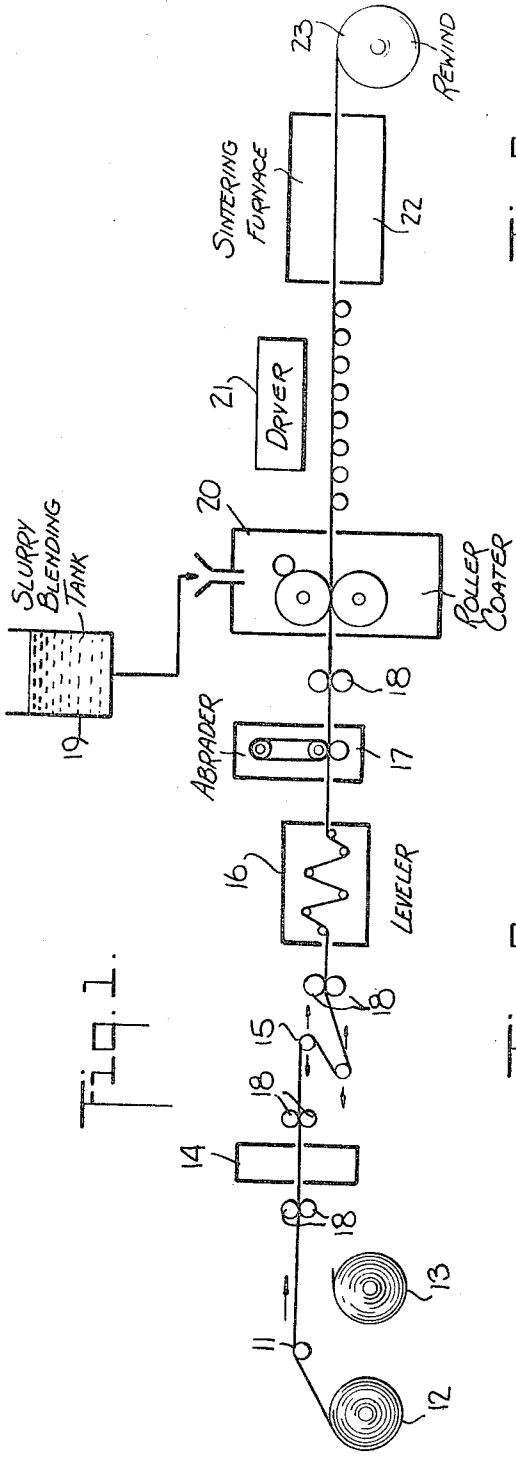

Fig. 1.

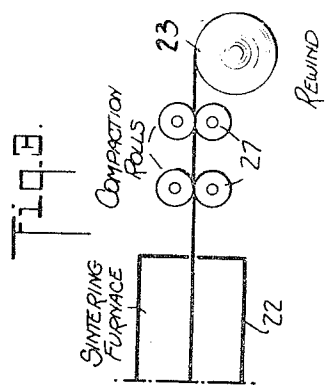

Fig. 3.

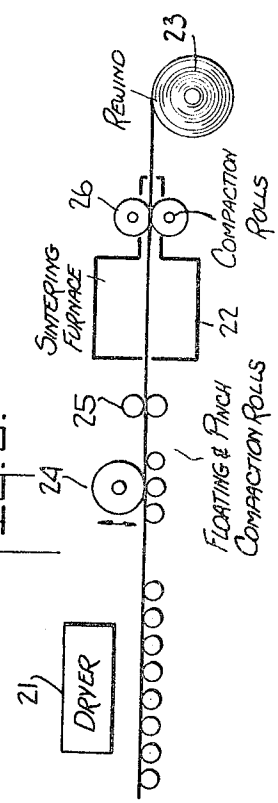

Fig. 2.

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Fig. 4.

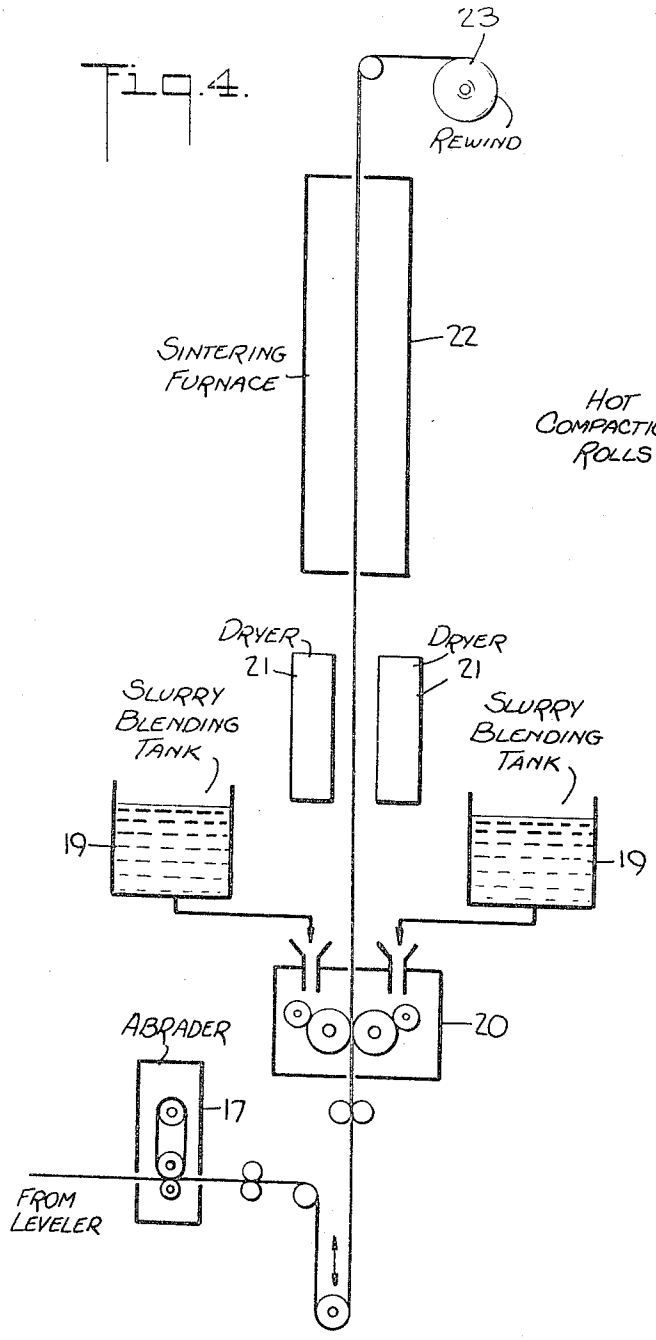
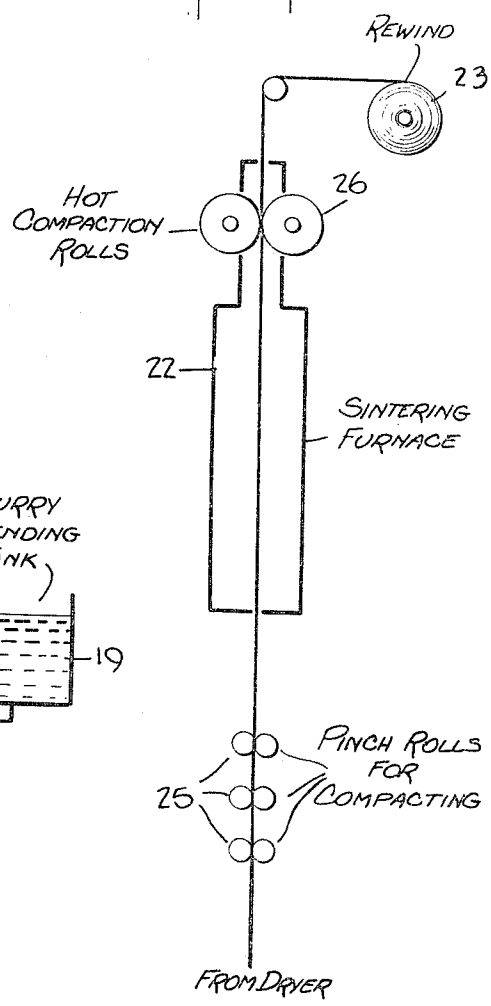


Fig. 5.



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PROCESS FOR PRODUCING NICKEL-COATED STEEL

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11 Claims. (Cl. 29—420.5)

This application is a continuation-in-part of our co-pending U.S. application Ser. No. 363,911 filed Apr. 30, 1964.

The present invention is directed to a method for producing relatively thin nickel coatings on steel and, more particularly, to an essentially continuous method for producing thin, dense, very uniform nickel coatings on steel strip using nickel powder as the source of nickel.

For many years it has been recognized that an economical method for producing thin, dense, corrosion resistant nickel coatings upon carbon and low alloy steel shapes such as strip, sheet and the like would be highly desirable in many industrial and consumer applications. Attempts have been made to effect this desirable result. Thus, a common method for applying thin nickel coatings to steel objects comprises the electroplating process. While this process has been used extensively in many applications, it is quite expensive and is not readily applicable to the economic production of nickel-coated steel in the form of long strips, large sheets and the like. Thus, in such instances, the capital investment required to install plants having sufficient capacity to yield a nickel coating about 2 mils thick upon long coils of steel strip or the like is so high that no such commercial installation can be installed with any prospect of recouping the required investment. Other means of applying nickel coatings, including flame spray coatings, are known but these methods also suffer serious disadvantages from the standpoint of cost and, further, it is difficult to produce thin coatings which are dense and free from pores through the use of such methods. The cladding of heavy steel plate with sheets of nickel, which are applied to the steel by means of welding and/or hot rolling, is also widely employed but such cladded steel plate is not economically produced at thicknesses of less than about ½ inch. It is also possible in connection with heavy plates and other heavy steel shapes to apply a nickel coating by welding methods. However, none of the foregoing methods is successful either from the standpoint of cost or from the standpoint of producing a thin, uniform coating substantially free from pores on thinner steel shapes such as sheet and strip which generally do not exceed about 0.165 inch in thickness. Accordingly, such nickel-coated steel materials are not now available commercially, although there are many industrial applications in which such materials could be usefully employed if they were made available at a suitable cost level.

A method has now been discovered whereby nickel coatings which are thin, dense, free from pores, and very uniform can be economically produced on a substantially continuous basis upon flat cold-rolled steel in a coil form, i.e., materials manufactured to strip and sheet tolerances, using nickel powder as the source of nickel.

It is an object of the present invention to provide a method for producing nickel-coated steel strip or sheet having a nickel coating which is thin, dense, and very uniform.

Another object of the invention is to provide an improved process for producing nickel coatings which are thin, uniform, and substantially free from pores upon long, thin, coilable steel shapes.

A still further object of the invention is to provide

sound, substantially pore-free nickel coatings on thin steel shapes.

A further object of the invention is to provide a method for nickel coating carbon and low alloy steel which may be employed in high speed modern steel mill lines with minimum disruption of the production scheme.

It is another object of the invention to provide an economical method for producing thin steel strip in coil form having a dense, protective nickel coating derived from a primary form of nickel.

Other objects and advantages of the invention will be made evident from the following description and the accompanying drawing in which:

FIGURE 1 is a representation of a method whereby a thin nickel coating is applied to coil steel strip;

FIGURE 2 is a modification of the representation set forth in FIGURE 1 wherein additional compaction steps are employed;

FIGURE 3 is a further modification of the modified method depicted in FIGURE 2;

FIGURE 4 is a representation depicting a method in accordance with the invention for coating coiled steel strip on both sides thereof wherein steel strip is transported vertically during the coating operations; and

FIGURE 5 depicts a modification of the methods illustrated in FIGURE 4 wherein additional compaction operations are employed before and after sintering of the nickel coating.

Broadly stated, the present invention comprises a method for producing a thin, dense nickel coating upon a thin, flat, coilable, strip-like steel shape having substantial length with respect to its width wherein at least one surface of the steel shape is treated to remove therefrom any rolled-in oxides and/or other surface imperfections; the thus-treated steel surface is then coated with an alkaline slurry containing about 50% to about 80%, by weight, of fine (i.e., less than about 10 microns average particle size) nickel powder, a small quantity, e.g., about 0.1% to about 5%, by weight, of a volatilizable organic binder or film former, a wetting agent, and a volatilizable vehicle; the thus-applied coating is then dried to remove the vehicle from the slurry coating; and the dried coating is then sintered in an atmosphere nonoxidizing to steel at a temperature of about 1300° F. to about 2200° F. or 2300° F., e.g., about 1800° F. to about 2100° F., for a time of about 15 seconds to about 90 minutes, e.g., about 20 seconds to about 10 minutes (with the shorter times being employed at the higher temperatures) to produce a sintered coating bonded to the steel and having sufficient adhesive and cohesive integrity that the strip-like steel shape at this point can be coiled. In order to effect the final compacting of the sintered nickel coating and to provide a finished nickel-coated flat steel strip-like shape, the sinter-coated steel is then subjected to one or more rolling operations and one or more annealing operations to provide the final product having a thickness range of generally about 0.015 to about 0.165 inch, having a dense, thin, strongly adherent nickel coating substantially free from pores, and having a nickel thickness generally in the range of about 0.5 to about 10 mils depending upon the initial thickness of nickel applied and the amount of cold reduction applied to the steel in the production scheme. Generally, the nickel coating provided in accordance with the invention will be about 2% to about 20% of the thickness of the nickel-coated article.

A slurry composition which is particularly useful for roller coating application to steel to produce uniform coatings comprises, on the basis of about 100 parts, by weight, of slurry, about 71 to about 75 parts, by weight, of fine nickel powder having an average particle size of about 2 to 5 microns, about 29 parts, by volume, of methyl cellulose as a 1% aqueous solution, a small

amount of a wetting agent to provide in the liquid portion of the slurry a surface tension of about 30 to 50 dynes per centimeter, with the slurry having a pH of not lower than about 8. It is to be understood, however, that the composition of the slurry and the viscosity thereof can be varied widely depending upon the coating technique to be employed. As will readily be understood, the viscosity of the slurry is reduced by reducing the quantity of nickel powder employed therein to amounts as low as about 50 parts, by weight, and, conversely, the viscosity of the slurry can be increased by increasing the quantity of nickel powder employed therein to amounts as high as about 80 parts, by weight. The viscosity of the slurry may also be increased by increasing the amount of organic binder or film former employed. Thinner, i.e., less viscous, slurries can be applied to the prepared steel strip surface by spraying and thicker, i.e., more viscous, slurries can be applied to the steel strip by a doctor blade technique. In general, slurries containing greater amounts of nickel provide thicker nickel coatings on the steel. In compounding the slurry, it is advantageous to subject the slurry to thorough mixing and permit it to stand for some time, e.g., several hours, to permit escape of entrapped air bubbles. The use of a wetting agent in the slurry is important and an amount of wetting agent is employed to decrease the surface tension of the slurry. Such agents also afford a measure of viscosity control in the slurry, facilitate adherence of the slurry to the steel strip, contribute a desirable leveling action to the slurry coating on the steel, and provide an improvement in the integrity of the final dense nickel coating. It is also important to control the pH of the slurry such that it is not lower than about 8 in order to prevent rusting of the steel during the time between application of the slurry mixture thereto and the completion of the drying operation. A source of hydroxyl ion is added to the slurry for this purpose. The hydroxyl ion source advantageously is ammonia or ammonium hydroxide, although other nitrogen bases such as the primary, secondary, tertiary and quaternary amines and other common reagents providing a basic reaction such as sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, etc., may also be employed. It is quite important to prevent rusting of the steel strip since it has been found that when rust is present or has formed on the steel before the sintering operation, it will contribute to the formation of pits and/or other types of undesirable discontinuities in the final nickel coating. It is also to be understood that heat-decomposable or volatilizable polymeric binders or film formers other than methyl cellulose which thicken water, which exert a stabilizing, dispersing, and anti-settling effect in the slurry, and which also yield low ash upon decomposition during the sintering operation may be employed in the slurry. Polyvinyl alcohol, starch, modified starch, chemically derivatized starch such as ethoxylated starch, cyanoethylated starch, etc., are examples of such materials. Binders or film formers assist in providing uniform initial nickel coatings on the steel and contribute green strength to the dried coating. Methyl cellulose is a very satisfactory binder from the standpoint of cost and efficacy and it is operable in an aqueous slurry containing nickel powder. The binder materials are of such a chemical nature that relatively small amounts in the vehicle, e.g., water, will provide a workable viscosity. For example, in the case of methyl cellulose, a proper viscosity for an aqueous roller coating slurry is obtained by employing about 0.15% to about 1%, by weight, of methyl cellulose in the slurry. The wetting agent, which can be of the nonionic, anionic or cationic type, and can be, for example, dioctyl sodium sulfosuccinate (sold under the trademark Aerosol OT), ethylene oxide condensation products of the primary fatty acids (sold under the trademark Ethomeen C–15), phosphorated higher alcohols (sold under the trademark Victawet 58–B), aliphatic substituted butyne diols and octyndiols (sold under the trademarks Surfynol 82 and Surfynol 104 E), dihexyl ester of sodium sulfosuccinic acid (sold under the trademark Aerosol MA), etc., is added to the other liquid ingredients of the slurry in an amount to control the surface tension of the liquid ingredients to the range of about 30 to about 50 dynes per centimeter. A dispersing or deflocculating agent, such as a sodium salt of a polycarboxylic acid (sold under the trademark Tamol) is also advantageous for purposes of aiding dispersion of the binder in the slurry. If it is found that the slurry exhibits undesirable foaming tendencies, a small addition of an anti-foaming or defoaming agent such as 2-octanol, a sulfonated oil or a silicone is made to the slurry to correct the condition. It is advantageous from many standpoints, including that of process economy, to employ an aqueous slurry, although the use of nonaqueous media (vehicles) in the slurry are also contemplated within the scope of the invention. Thus, various organic solvents can be employed as vehicles in the slurry for the purpose of dissolving or dispersing the film former or binder employed therein. Satisfactory vehicles include various alcohols, including methanol, ethanol, propanol, butanol, furfuryl alcohol, benzyl alcohol, etc., ketones, including methyl ethyl ketone, acetone, methyl isobutyl ketone, etc., formamide, dimethyl formamide, ethylene glycol, etc.

The drying operation can be conveniently carried out by means of gas-fired infrared heaters. It is also to be understood that satisfactory atmospheres which may be employed during the first sintering operation may comprise atmospheres derived from cracked ammonia, dry hydrogen and the like.

It is contemplated that the invention will be particularly applicable in conventional steel mill practice at the "hot band" stage of steel strip manufacture. At this point in the steel mill production scheme, the steel strip commonly has a thickness in the range of about 0.05 inch to about 0.25 inch and is readily coilable. Hence, coils of hot-rolled steel strip can be removed from the circuit, can be appropriately surface treated and coated with the nickel-sinter coating described hereinbefore, and can then be returned to the regular mill production scheme for finishing by cold rolling and annealing to provide nickel-coated steel strip having the desired thickness and having a dense nickel coating about 0.5 to 10 mils thick essentially free from pores.

For the purpose of illustrating the application of the invention to the nickel coating of steel mill hot bands, reference is now made to the accompanying drawing. In the drawing, FIGURE 1 depicts schematically one embodiment of a method whereby steel mill hot bands are coated with a nickel-sinter coat in accordance with the invention and are thus prepared for return to the steel mill production scheme at the hot band stage. In the drawing, **11** depicts a payoff machine holding coils of descaled steel strip, e.g., pickled hot bands, **12** and **13** which pass to a welder **14** adapted for the purpose of welding ends of the hot band coils together. The strip can then pass through a looper or looping pit **15** to obtain constant speed in the line. A leveler **16** adapted to correct minor shape irregularities in the steel hot bands desirably is employed. The hot band is subjected to treatment in an abrading machine as depicted at **17** to remove from at least one side of the steel strip minor discontinuities, oxides, mill defects, etc. Feeder rolls **18** can be disposed between the various machines. A slurry blending tank **19** can be employed to mix aqueous nickel powder slurry which is fed to roller coater device **20** adapted to coat at least one side of the steel hot band being treated with an aqueous slurry containing nickel powder and having the composition set forth hereinbefore. The coated band is then dried and this can be accomplished in dryer **21** which advantageously comprises a series of infrared gas burners operated at a surface temperature of about 1400° F. and adapted to raise the temperature of the

ing. Proper pH control, as exemplified by the use of a small ammonia addition to insure an alkaline state in the initial slurry mixture is also important for the same reason. Ammonia is a most attractive compound for the purpose of pH control because it is highly effective, leaves no ash, and is quite inexpensive. It is also to be understood that roll compaction of the sintered nickel coating is essential in order to provide the final fully dense nickel coating contemplated in accordance with the invention. It has been found that if any of the aforementioned important ingredients or controls is omitted from the initial slurry, much less satisfactory results are obtained in the final nickel coating and the incidence of defects in the final coating is increased.

The special process contemplated in accordance with the invention wherein both a wetting agent and an agent for effecting pH control is employed in the initial slurry yields a final nickel-coated steel strip having essentially no defects in the coating as revealed by the "hot water" porosity test. This test has been found to be a very searching test for defects in thin nickel coatings on steel and comprises immersing specimens in continuously aerated pure water maintained at a minimum temperature of 185° F. for 1 to 6 hours, depending upon the coating thickness with longer times being used for thicker coatings.

It is highly advantageous in accordance with the invention to employ fine carbonyl nickel powder having a particle size in the range of up to about 10 microns, e.g., about 2 to 5 microns. It appears such high purity powders are uniquely applicable in the process, especially when the roller coating technique is employed in initially applying the nickel-containing slurry to the prepared steel strip. It is contemplated that coarser nickel powders having lower purity than carbonyl nickel powder might be employed but it is then necessary to employ higher sintering temperatures, longer sintering times, and greater amounts of reduction in the rolling operations in order to obtain the required high density and freedom from porosity in the final nickel coating contemplated in accordance with the invention. It is also contemplated and, in some instances, it is quite desirable to replace up to about 65% or about 75% by weight of the initial nickel powder with fine copper powder, e.g., copper powder of the minus 325 mesh grade. In such instances, nickel-copper alloy coatings are produced which are advantageous in certain environments.

It will be appreciated that the process contemplated in accordance with the invention can be carried out either in a continuous or a semicontinuous fashion. The sinter-coated strip has sufficient integrity to be coiled. Accordingly, the further compacting and annealing steps employed as described hereinbefore to produce the final nickel-coated strip having 100% of theoretical density can be carried out either batchwise or in a continuous line. In many installations, it is advantageous to carry out the rolling and annealing operations in batches. Thus, conventional batch-type furnaces in which coils of strip can be stacked, and a protective atmosphere maintained therein during the annealing operation, may be employed. Advantageously, the "open-coil" annealing system is employed as otherwise steps must be taken to prevent sticking of the coil faces.

The final product in accordance with the invention can be welded, drawn, or formed without losing the protective character of the nickel coating. Nickel-coated articles stamped or otherwise formed from nickel-coated steel produced in accordance with the invention can be coated with chromium for decorative purposes as by electrodeposition or otherwise.

When the term "steel" is employed herein, it is to be understood that reference is made to common grades which are processed in continuous fashion, including low and medium carbon steels, such as deep drawing grades and the like and to low alloy steels.

The nickel-coated strip may be employed in many commercial markets in which appearance of the finished product is an important selling point. Such markets include appliances, automotive trim and bumpers, furniture, office equipment, etc. Other applications include those in which product protection is essential such as food and chemical processing and handling equipment. Thus, evaporators, containers, mixers and many other pieces of equipment employed in processing such product lines may be fabricated from nickel-coated steel provided in accordance with the invention.

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. The process for applying a sound, dense nickel coating to hot-rolled steel strip using fine nickel powder as the source of nickel which comprises the steps of:
   (a) treating at least one surface of a hot-rolled steel strip to be coated to remove oxides and other defects therefrom,
   (b) coating the treated surface of the steel strip with an alkaline slurry containing about 50% to about 80%, by weight, of metal powder consisting of, on the basis of metal powder weight, up to about 75% of copper powder and the balance essentially nickel powder, with the balance consisting essentially of at least one liquid vehicle, a polymeric binder dispersible in the vehicle, and a wetting agent,
   (c) drying the slurry coating to substantially remove the vehicle therefrom,
   (d) sintering the resulting dried coating in an atmosphere nonoxidizing to steel at a temperature of about 1300° F. to about 2300° F. for at least about 15 seconds up to about 90 minutes to provide nickel sinter-coated strip, and
   (e) subjecting the nickel sinter-coated strip to at least one compaction operation.

2. The process according to claim 1 wherein the nickel sinter-coated steel strip is subjected to compacting at a temperature from room temperature up to about 1900° F. to provide a density of at least about 80% in the coating without substantial reduction of the steel, and the thus-treated strip is subjected to at least one cold-rolling and at least one annealing to provide substantially 100% density in the nickel coating.

3. The process according to claim 1 wherein the dried strip after step (c) is subjected to at least one compacting operation prior to step (d).

4. The process according to claim 1 wherein the slurry employed in step (b) has a pH not lower than about 8 and contains, by weight, about 50% to about 80% of carbonyl nickel powder having a particle size of less than about 10 microns, a binder from the group consisting of methyl cellulose, polyvinyl alcohol, starch, modified starch and chemically derivatized starch, a wetting agent to provide a surface tension of about 30 to about 50 dynes per centimeter, and the balance essentially water.

5. The process according to claim 4 wherein the slurry contains about 0.1% to about 5%, by weight, of binder.

6. The process according to claim 1 wherein the slurry employed in step (b) consists essentially of about 71 to about 75 parts, by weight, of carbonyl nickel powder having a particle size of about 5 to about 8 microns, about 29 parts, by volume, of methyl celluose as a 1% aqueous solution, a small amount of a wetting agent to provide in the liquid portion of the slurry a surface tension of about 30 to 50 dynes per centimeter, and about 1 part, by volume, of ammonium hydroxide.

7. The process according to claim 1 wherein the sinter-

ing in step (d) is conducted at a temperature of about 1800° F. to about 2100° F. for a time of about 20 seconds to about 10 minutes.

8. The process according to claim 6 wherein roller coating is employed to apply the slurry to the strip.

9. The process for applying a sound, dense nickel coating to steel strip using fine nickel powder as the source of nickel which comprises the steps of:

(a) coating a prepared surface of a steel strip with an alkaline slurry containing about 50% to about 80%, by weight, of metal powder consisting of, on the basis of metal powder weight, up to about 75% of copper powder and the balance essentially nickel powder, with the balance of said slurry consisting essentially of at least one liquid vehicle, a polymeric binder dispersible in said vehicle, and a wetting agent,

(b) drying the resulting slurry coating to substantially remove said vehicle therefrom,

(c) sintering the dried coating in an atmosphere nonoxidizing to steel at a temperature of about 1300° F. to about 2300° F. for a time sufficient to effect sintering of the nickel coating and bonding thereof to said steel,

(d) hot compacting the resulting sintered coating to a density of at least about 90% of theoretical density at a temperature of about 800° F. to about 1900° F. while maintaining a nonoxidizing atmosphere about said coated strip, and

(e) cooling the resulting strip having the hot compacted nickel coating thereon in a nonoxidizing atmosphere to provide a nickel-coated steel strip suitable for cold rolling in usual steel mill equipment.

10. The process for applying a sound, dense nickel coating on steel strip using fine nickel powder as the source of nickel which comprises the steps of:

(a) coating a prepared surface of a steel strip with an alkaline slurry containing about 50% to about 80%, by weight, of fine nickel powder, with the balance of said slurry consisting of at least one liquid vehicle having a polymeric binder dispersed therethrough,

(b) drying the resulting slurry coating to substantially remove said vehicle therefrom,

(c) sintering the dried coating in an atmosphere nonoxidizing to steel at a temperature of about 1700° F. to about 1950° F. for a time sufficient to effect sintering of the nickel coating and bonding thereof to said steel,

(d) hot compacting the resulting sintered coating to a density of at least 90% of theoretical density by rolling said strip at a temperature of at least about 1400° F. while maintaining a nonoxidizing atmosphere about said coated strip, and

(e) cooling the resulting strip having the hot compacted nickel coating thereon in a nonoxidizing atmosphere to provide a nickel-coated steel strip suitable for cold rolling in usual steel mill equipment.

11. The process according to claim 10 wherein carbonyl nickel powder is employed in preparing the slurry of step (a).

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