

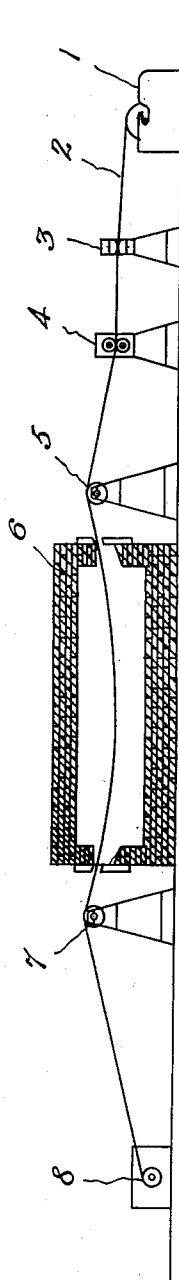
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C. G. CROCKER ET AL

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PROCESS OF PRODUCING COLORED OXIDE COASTINGS ON NICKEL AND NICKEL ALLOYS

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PROCESS OF PRODUCING COLORED OXIDE
COATINGS ON NICKEL AND NICKEL
ALLOYS

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The present invention relates to a process of producing oxide coatings of various colors on nickel and nickel alloys, and more particularly to a process of producing such oxide coatings by heating the nickel or nickel alloy articles under controlled conditions of atmosphere, temperature and duration of treatment to form the desired colored oxide coating.

It is an object of the present invention to provide a process of producing oxide coatings of desired color on nickel and nickel alloys.

It is another object of the invention to provide a process of producing uniformly colored adherent oxide coatings of desired color on nickel and nickel alloys which can be carried out on an industrial scale.

It is a further object of the invention to provide a process of consistently producing uniformly colored adherent oxide coatings of desired color on nickel and nickel alloys on an industrial scale.

Other objects and advantages of the present invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawing which represents schematically a strip oxidizing apparatus suitable for carrying out the process of the present invention.

Referring to the drawing, reference numeral 1 represents a coil box adapted to receive a coil of strip to be treated. This strip, designated by reference numeral 2, passes first through dry cloth wipers 3, then through a pair of pinch rolls 4 which uncoil the strip 2 at a controllable rate and pass it over a supporting roll 5 into a furnace 6. The furnace 6 may be of any suitable type. In the drawing it is represented as a gas fired catenary furnace with open ends, but any other suitable type of furnace may be used, as those skilled in the art will readily understand. Near the withdrawal end of the furnace is a second supporting roll 7 similar to roll 5, and between these two supporting rolls the strip 2 hangs as a catenary. A take-up drum 8 is driven at a controllable rate to maintain the proper tension on the strip and to recoil the strip after treatment.

In the case of sheet, a closed type sheet furnace may be used for the oxidizing treatment. In the present description the term "strip" is

used to denote products processed continuously or in long lengths and the term "sheet" is used to denote products produced in shorter lengths which may be placed completely within furnaces. Thus, the strip material 2 shown in the drawing may be cut into sheets subsequent to passing continuously through the furnace or cut into sheets prior to the oxidizing treatment and the sheets given an oxidizing treatment in a sheet or batch furnace. Furnaces built for the treatment of strip material which extends through the furnace will often differ in construction from furnaces built for the treatment of sheet material which may be placed completely within the furnace as those skilled in the art will readily understand.

Generally speaking, the process of the present invention comprises the steps of melting, refining, casting, forging, hot rolling, cold rolling, annealing and optionally pickling the nickel or nickel alloys preparatory to introducing the same into the furnace where the colored coating is produced under controlled conditions of temperature, time of exposure, atmosphere, etc. The color of the oxide coating produced depends not only upon the temperature, atmosphere and duration of the oxidizing treatment but upon the composition of the metal or alloy as well. In order to obtain consistent results, it is necessary to control the temperature and duration of treatment within relatively narrow limits and to correlate these with each other and with the composition of the metal being treated. For example, a lustrous blue-black coating can be imparted to nickel containing a minimum of about 2% manganese under conditions which produce a brown oxidized coating on nickel of approximately the following composition: 99.4% nickel, 0.10% copper, 0.15% iron, 0.15% manganese and 0.10% silicon. By varying the conditions of the treatment somewhat, the last mentioned alloy can be given a green oxidized coating instead of brown.

The temperature used to produce the desired colored oxidized coating and the duration of the heating depend upon the thickness of the metal being treated and also upon each other. In general, if a higher temperature is used the duration of the treatment of a given piece of metal or alloy would be shortened and vice versa. Simi-

larly, if a thicker piece is to be treated the temperature and/or duration of heating must be appropriately increased.

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

EXAMPLE NO. I

Blue-black oxidized nickel sheet

A 14" x 14" ingot having about 97.7% nickel, 2.00% manganese, 0.10% iron, 0.005% sulphur and 0.08% carbon was forged at a temperature of about 2250° F. to 4" x 11" blooms which were rolled at a temperature of about 2200° F. to sheet bar approximately 3/4" x 1 1/2" x 39". Hot rolled sheets were produced from the bars by roughing down and finishing on a hot sheet mill in the usual manner to sheets approximately

0.039" x 39" x 72"

The hot rolled sheet thus obtained was reduced in thickness to about 0.037" by cold rolling and then annealed for about five minutes at about 1650° F. in a reducing atmosphere containing approximately 4.0% carbon monoxide. The annealed sheet was thereafter pickled in a hot sulphuric acid-sodium nitrate pickling solution. The pickled sheet, which was free from scale, oxides, etc. and had a bright, smooth metallic surface, was next subjected to an oxidizing treatment. A gas-fired sheet furnace heated to a temperature of about 1800° F. was utilized for the oxidizing treatment which lasted for about one minute twenty seconds. The atmosphere, by Orsat analysis, comprised about 2.5% oxygen and 10.5% carbon dioxide. A dark blue-black adherent oxide coating was produced.

The composition may vary from about 95% to 98% Ni and about 2% to 5% Mn.

The furnace temperature may vary from about 1700° F. to about 1850° F. depending upon the thickness of the metal object. Similarly, the time of exposure in the furnace may vary from about one to about four minutes. Illustrative examples of these relationships are set forth in Schedule I.

SCHEDULE I*

Thickness of metal	Furnace temperature	Time of exposure	Furnace atmosphere
<i>Inches</i> 0.062 0.060	<i>°F.</i> 1820 1780	3 min., 20 sec. 2 min.	2.5% O ₂ :10.5% CO ₂ 3.5% O ₂ :8.5% CO ₂

*A natural gas-fired sheet furnace was used for these examples.

In both cases the color of the oxide coating was practically the same as the 0.037" sheet that was heated for 1 minute 20 seconds at 1800° F.

EXAMPLE NO. II

Green oxidized nickel sheet

An ingot having approximately the following composition 99.5% nickel, .15% manganese, .15% iron, .005% sulphur and .07% carbon was worked to sheet and treated in the same manner as the metal of Example No. I.

Due to the difference in composition the oxide coating was green rather than blue-black. The composition may vary within the following limits

and still yield a green oxide coating when treated as set forth hereinabove in Example No. I:

	Per cent	Per cent
Nickel.....	About 98.33	to about 99.98
Manganese.....	Trace	to about 1.00
Iron.....	About .01	to about .25
Copper.....	About .005	to about .20
Silicon.....	None	to about .05
Sulphur.....	.001	to about .015
Carbon.....	None	to about .15

The furnace temperature may vary from about 1700° F. to about 1850° F. depending upon the thickness of the metal object. Similarly the time of exposure in the furnace may vary from about one to about four minutes.

EXAMPLE NO. III

Green oxidized nickel strip

The metal used had the same composition as that used in Example No. II. The preliminary treatment involved hot forging a 14" x 14" ingot at about 2250° F. to 8" x 8" blooms, hot rolling the blooms at about 2250° F. to billets 3" x 4 1/2", and the billets thus produced to strip about

0.125" x 5"

The strip was annealed at about 1350° F., pickled in a sulphuric acid-sodium nitrate solution and cold rolled to about 0.050" gauge; annealed again at 1350° F. and cold rolled to about 0.021" gauge. The cold rolled strip was coiled and placed in the coil box 1 of the apparatus illustrated in the drawing. From there it was passed through the dry cloth wipers 2, pinch rolls 4, over supporting roll 5 and then through the oxidizing catenary furnace 6 maintained at a temperature of about 2000° F. The strip was exposed for about one minute in an atmosphere containing about 5.0% oxygen and 8.0% CO₂ by Orsat analysis. A beautiful green adherent coating was produced. The temperature range extends from about 1700° F. up to about 2100° F.

The thickness of the metal, time of exposure and furnace conditions may vary as illustrated in Schedule II.

SCHEDULE II

Thickness of metal	Furnace temperature	Time of exposure	Furnace atmosphere
.010" .025"	°F. 2000 2100	1 min. 40 sec.	5.1% O ₂ :8.0% CO ₂ 4.7% O ₂ :10.0% CO ₂

EXAMPLE NO. IV

Brown oxidized nickel sheet

The metal used had the same composition as that used in Example No. II, and it was worked in the same manner to sheet approximately 0.039" x 39" x 72". The hot rolled sheet thus obtained was cold rolled to .037" and then oxidized by exposing it in a continuous type sheet furnace at a temperature of about 1500° F. for about three minutes. The atmosphere was composed of about 3.5% O₂ and 9.5% CO₂ by Orsat analysis. An adherent brown oxidized coating was produced. A temperature up to about 1800° F. may be used.

EXAMPLE NO. V

Blue-black oxidized nickel-copper alloy strip

Nickel-copper alloys having about 2/3 nickel

and $\frac{1}{3}$ copper, sold commercially under the trade-mark "Monel," are widely used where rust immunity and corrosion resistance are essential. In commercial practice the copper content ordinarily amounts to at least about 23% and the nickel content to at least about 60%. Other elements such as iron, manganese, silicon, aluminum, carbon etc., may also be present, as those skilled in the art know. It has been found that such an alloy when given a blue-black oxide coating is a particularly suitable material for heat deflectors of electric range units and similar heaters because it combines rust immunity and corrosion resistance with ability to resist discoloration from relatively high temperature, e. g., up to about 1400° F. The metal containing approximately 67.07% nickel, 30.28% copper, .15% carbon, 1.04% manganese, 1.34% iron, 0.005% sulphur and 0.06% silicon was prepared for the oxidizing treatment by forging a 14"x14" ingot at about 2200° F. to 3"x7 $\frac{1}{2}$ " slabs and hot rolling the slabs at about 2150° F. to 0.125"x8" strip. The strip was then annealed at 1400° F. pickled in a sulphuric acid-sodium nitrate solution and cold rolled to .045" gauge, annealed as before, and cold rolled to .021" gauge. The cold rolled strip was coiled and placed in the coil box 1 of the apparatus shown in the drawing. From there it was passed through the dry cloth wipers 3 and then through the oxidizing gas-fired catenary furnace 6 maintained at a temperature of about 1550° F. An exposure of about 50 seconds was necessary in an atmosphere of 10.0% O₂, 5.0% CO₂, by Orsat analysis, to produce the adherent blue-black oxide coating. Satisfactory results have been obtained under the conditions set forth in Schedule III.

SCHEDULE III

Furnace type	Thickness of metal	Furnace temperature	Time of exposure	Furnace atmosphere
Gas-fired catenary.....	.021"	°F. 1550	Seconds 50	10.0% O ₂ ; 4% CO ₂
Do.....	.031"	1650	50	9.0% O ₂ ; 6% CO ₂

The temperature may go as high as about 1900° F.

EXAMPLE NO. VI

Blue-black oxidized nickel-copper alloy sheets

The metal used had about the same composition as that used in Example No. V and was prepared for the oxidizing treatment by forging a 14"x14" ingot at about 2200° F. to 4"x11" blooms which were rolled at a temperature of about 2200° F. to sheet bar approximately $\frac{3}{8}$ "x11 $\frac{1}{2}$ "x39". Hot rolled sheets were produced from the bars by roughing down and finishing on a hot sheet mill in the usual manner to sheet approximately .039"x39"x72". The hot rolled sheet thus obtained was reduced in thickness to .037" by cold rolling and then annealed for about five minutes at about 1750° F. in a reducing atmosphere containing approximately 4% carbon monoxide. The annealed sheet was thereafter pickled in a hot sulphuric acid-sodium nitrate pickling solution. The pickled sheet, which was free from scale, oxides, etc., and had a bright, smooth metallic surface, was next subjected to an oxidizing treatment. A gas-fired sheet furnace heated to a temperature of about 1800° F. was utilized for the oxidizing treatment which lasted for about sixty seconds. The atmosphere, by Orsat analysis, comprised about 3.0% oxygen

and 10% carbon dioxide. A dark blue-black adherent oxide coating was produced.

The furnace temperature may vary from about 1700° F. to about 2000° F. depending upon the thickness of the metal object. Similarly, the time of exposure in the furnace may vary from about one-half to about three minutes. Illustrative examples of these relationships are set forth in Schedule IV.

SCHEDULE IV*

Thickness of metal	Furnace temperature	Time of exposure	Furnace atmosphere
Inches .021	°F. 1850	50 sec.	2.1% O ₂ ; 10.9% CO ₂
.031	1900	1 min., 16 sec.	2.1% O ₂ ; 10.9% CO ₂

* A natural gas-fired sheet furnace was used for these examples.

EXAMPLE NO. VII

Black oxidized nickel-chromium-iron alloy sheet

Alloys of this type may contain about 70.00% to 80.00% nickel, about 11.00% to 15.00% chromium and about 5.0% to 10.0% iron and are sold under the trade-mark "Inconel." A 14" x 14" ingot of this metal was hot forged at 2300° F. to sheet bar about $\frac{3}{8}$ " x 11 $\frac{1}{2}$ " wide x 39". Hot rolled sheet was produced from the bars by roughing down and finishing on a hot sheet mill in the usual manner to sheet about .039" x 39" x 72". The hot rolled sheet was cold rolled to about .037" thick, annealed at 1800° F. for about four minutes, and pickled in a sulphuric acid-sodium nitrate pickling solution. Satisfactory adherent black coatings have been obtained under the conditions set forth in Schedule V.

SCHEDULE V*

Furnace type	Thickness of metal	Furnace temperature	Time of exposure	Furnace atmosphere
Gas-fired sheet.....	Inches .037	°F. 1850	1 min. 30 sec.	3.5% O ₂ 8.5% CO ₂
Do.....	.062	2000	2 min.	3.0% O ₂ 8.2% CO ₂

*The temperature may go as high as about 2200° F.

The sheet and strip, when colored as taught hereinbefore, may be fabricated into a wide variety of useful and attractive articles. The nickel and nickel alloys are inherently immune to rust and resistant to corrosion, and in the colored condition may generally be used where the plain metal has been found useful with the added advantage of color stability. The latter property is particularly advantageous in applications where the metal becomes heated in use. Common examples include deflector or reflector pans for heating elements on electric ranges, burner bowls on gas ranges, sheathing of electric heating elements, laboratory oven linings, etc. Railroad car roofs may be mentioned as an example of a field of general utility where resistance to corrosion is advantageous. The firm adherence of the colored oxide coating produced by the present invention permits the colored oxide coated sheet and strip to be formed and shaped into fabricated products without cracking or flaking the adherent colored oxide coating. The colored nickel and nickel alloys of the present invention may also be applied where the color is used for decorative purposes, e. g., camera cases, clock hands, gauge pointers, etc.

In the above examples specific conditions of rolling, annealing and pickling have been given but it will be understood that modification of these conditions within certain limits is possible, as those skilled in the art will understand. Moreover, the surfaces to be coated may be prepared for the oxidizing treatment by methods other than cold rolling and pickling. For example, surfaces that had been cleaned or freed from scale, etc., by sand blasting, by grinding, by electrolytic cleaning or by various other cleaning methods have been given satisfactory adherent colored oxide coatings by subjecting the metal or alloy to oxidizing atmospheres under conditions comparable to the specific examples given hereinbefore.

Although the specific examples have illustrated the invention as applied to the coloring of sheet and strip material, it will be readily understood by those skilled in the art that the invention may also be used for applying colored oxide coatings to nickel and nickel alloy rods, tubes, bars, and other shapes and forms. Such shapes and forms are to be understood as coming within the scope of the foregoing description and the appended claims.

We claim:

1. The process of producing adherent blackish uniformly colored oxide coatings on rolled products of nickel alloys selected from the group consisting of nickel-manganese alloys containing about 2% to about 5% manganese and the balance substantially all nickel, nickel-copper alloys containing about 30% copper, about 1% manganese, about 1% iron and the balance substantially all nickel, and nickel-chromium-iron alloys containing about 11% to about 15% chromium, about 5% to about 10% iron and the balance substantially all nickel which comprises exposing the cleaned rolled product to a heated oxidizing atmosphere effective to produce a uniform blackish oxide coating on the surface thereof while maintaining said product at selected elevated temperatures within the range of about 1550° F. to about 2200° F. for a period of time of the order of about ½ minute to about 4 minutes whereby rolled nickel alloy products are produced having an adherent blackish coating characterized by uniformity and stability of color.

2. The process of producing an adherent blue-black uniformly colored coating on a rolled product made of an alloy containing about 30% copper, about 1% manganese, about 1% iron and the balance substantially all nickel which comprises exposing the clean rolled product to a heated oxidizing atmosphere effective to produce a uniform blue-black oxide coating on the surface thereof while heating said product at selected elevated temperatures within the range of about 1550° F. to about 2000° F. for a period of time of the order of about ½ minute to about 4 minutes whereby a rolled nickel-copper alloy product is produced having an adherent blue-black coating characterized by uniformity and stability of color.

3. The process of producing an adherent blue-black uniformly colored oxide coating on a strip made of an alloy containing about 30% copper, about 1% manganese, about 1% iron and the balance substantially all nickel which comprises exposing the clean strip to a heated oxidizing atmosphere effective to produce a uniform blue-black oxide coating on the surface thereof while heating said strip at selected elevated tempera-

tures within the range of about 1500° F. to about 1900° F. for a period of time of the order of about 1 minute whereby a rolled nickel-copper alloy strip is produced having an adherent blue-black coating characterized by uniformity and stability of color.

4. A process of producing a blue-black uniformly colored coating on a cold rolled strip made of an alloy containing about 30% copper, about 1% manganese, about 1% iron and the balance substantially all nickel which comprises placing cold rolled strip into a gas fired catenary furnace having a heated oxidizing atmosphere effective to produce a uniform blue-black oxide coating on the surface thereof, heating the strip to temperatures within a range of about 155° F. to 1900° F. for about 1 minute, whereby strip of nickel-copper alloy is produced having an adherent blue-black coating characterized by uniformity and stability of color.

5. Process of producing an adherent blue-black, uniformly colored coating on a rolled product made of an alloy containing about 2% to about 5% manganese and about 95% to about 98% nickel which comprises exposing the clean rolled product to a heated oxidizing atmosphere effective to produce a uniform blue-black oxide coating on the surface thereof while heating said product at selected elevated temperatures within the range of about 1700° F. to about 1850° F. for a period of time of the order of about 1 minute to about 4 minutes whereby a rolled nickel-manganese alloy product is produced having an adherent blue-black coating characterized by uniformity and stability of color.

6. A process of producing an adherent blue-black uniformly colored coating on rolled sheet made of an alloy containing about 2% to about 5% manganese and about 95% to about 98% nickel which comprises exposing pickled rolled sheet to a heated oxidizing atmosphere effective to produce a uniform blue-black oxide coating on the surface thereof while heating said sheet at selected elevated temperatures within the range of about 1700° F. to about 1850° F. for a period of time of the order of about 1 minute to about 4 minutes whereby a rolled nickel manganese alloy sheet is produced having an adherent blue-black coating characterized by uniformity and stability of color.

7. A process of producing an adherent black uniformly colored coating on a rolled product made of an alloy containing about 11% to about 15% chromium, about 5% to about 10% iron and the balance substantially all nickel which comprises exposing the clean rolled product to a heated oxidizing atmosphere effective to produce a uniform black oxide coating on the surface thereof while heating said product at selected temperatures within the range of 1850° F. to about 2200° F. for a period of time of the order of about 1 minute to about 2 minutes whereby a rolled nickel-chromium-iron alloy product is produced having an adherent black coating characterized by uniformity and stability of color.

8. The process of producing an adherent black uniformly colored coating on rolled sheet made of an alloy containing about 11% to about 15% chromium, about 5% to about 10% iron and the balance substantially all nickel which comprises exposing pickled rolled sheet to a heated oxidizing atmosphere effective to produce a uniform black oxide coating on the surface thereof while heating said sheet at selected elevated tempera-

tures within the range of about 1850° F. to about 2200° F. for a period of time of the order of about 1 minute to about 2 minutes whereby a rolled nickel-chromium-iron alloy sheet is produced having an adherent black coating characterized by uniformity and stability of color.

5 9. The process of producing an adherent blue-black uniformly colored coating on nickel base alloy containing about 23% up to about 33%
10 copper comprising exposing clean worked pieces of the alloy to a heated oxidizing atmosphere effective to produce a uniform blue-black oxide coating on the surface thereof maintained at selected elevated temperatures within the range
15 of about 1500° F. to about 2000° F., and maintaining said pieces in said heated oxidizing atmosphere until the surface thereof has been at oxidizing temperature for a period of time of the order of about ½ minute to about 4 minutes whereby an adherent blue-black coating is

produced characterized by uniformity and stability of color.

10. The process of producing an adherent blue-black uniformly colored coating on nickel base alloy containing about 23% up to about 33%
5 copper comprising exposing clean worked pieces of the alloy to a heated oxidizing atmosphere effective to produce a uniform blue-black oxide coating on the surface thereof maintained at selected elevated temperatures within the range
10 of about 1500° F. to about 2000° F., and maintaining said pieces in said heated oxidizing atmosphere for an accentuatedly short period of time of the order of about ½ minute to about four minutes sufficient to produce an adherent
15 blue-black coating on the surface thereof characterized by uniformity and stability of color.

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CERTIFICATE OF CORRECTION.

Patent No. 2,206,392.

July 2, 1940.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, line 16, claim 4, for "155° F." read --1550° F.--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of September, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.