

**IMPROVED PROCESS FOR COLORING
LOW TEMPERATURE CARBURIZED AUSTENITIC STAINLESS STEEL**

Related Applications

[0001] This application claims the benefit of United States Provisional patent application serial number 60/773,497 filed on February 15, 2006 for Improved Process for Coloring Low Temperature Carburized Austenitic Stainless Steel, the entire disclosure of which is fully incorporated herein by reference.

Background and Summary

[0002] U.S. Patent No. 5,792,282, as well as commonly assigned U.S. Patent No. 6,547,888 B1, the disclosures of which are incorporated herein by reference, describe processes for increasing the hardness of austenitic stainless steel workpieces by low temperature carburization, i.e., carburization carried out in such a way that a hardened surface or "case" is formed which is rich in diffused carbon but substantially free of corrosion-promoting carbide precipitates.

[0003] Meanwhile, commonly assigned Provisional Application 60/653,147, filed February 15, 2005, and Non-Provisional Application 11/272,915 the disclosures of which are also incorporated herein by reference, describes stainless steel tube fittings and ferrules which are color coded for easy identification. Color coding is accomplished by growing a colored oxide coating on the workpiece surfaces, either

thermally (i.e., by heating in the presence of an oxygen-containing gas) or electrochemically.

[0004] This technology is described as being applicable to conventional or “native” stainless steels, as well as low temperature carburized austenitic stainless steels such as described in the above ‘282 and ‘888 patents. In practice, however, it has been found that colorizing low temperature carburized stainless steel by known electrochemical processes is essentially ineffective in that no substantial color change occurs.

[0005] It has now been found that a low temperature carburized stainless steel workpiece can be carburized to a wide spectrum of different intense colors by cleaning the workpiece so as to remove the porous oxide layer inherently formed during low temperature carburization and then subjecting the electropolished workpiece to alternating current electrolysis in an electrolysis bath which contains a metal having multiple valence states and which further is maintained at a neutral to slightly basic pH.

BRIEF DESCRIPTION OF THE DRAWING

[0006] The present invention may be more readily understood by reference to the Drawings and Detailed Description.

[0007] Fig. 1 illustrates a prior art fitting in a finger tight position;

[0008] Fig. 1A illustrates the fitting of Fig. 1A in a tightened position; and

[0009] Fig. 2 is a schematic illustration of the waveform of the electrical current applied to the workpiece in accordance with one embodiment of the invention.

DETAILED DESCRIPTION

Tube Fittings and Ferrules

[0010] Tube fittings are well known articles of commerce. In this application, the term “tube fitting” means any type of tube fitting, unless otherwise stated. Examples of tube fittings include, but are not limited to, ferrule type fittings, such as single ferrule fittings, two ferrule fittings, and fittings that include more than two ferrules, flared tube end fittings, and other types of fittings. Examples of ferrule type fittings are described, for example, in commonly assigned US Patent Nos. 3,103,373, 6,629,708, provisional

application Serial No. US60/652,631 (attorney docket no. 22188/06884), and PCT application PCT/US06/03909 the disclosures of which are incorporated herein by reference in their entirety. Typically, a fitting is composed of various components including body sections, nuts, ferrules or "gripping rings," and the like. A ferrule may be designed so that, during pull-up, it plastically deforms, or its leading edge bites into the conduit being joined, or both. A ferrule may also be designed so that, during pull-up, the ferrule does not bite into the conduit being joined. In accordance with this invention, such fittings (and/or component parts thereof) are color coded electrolytically for easy identification by growing a colored oxide coating on one or more surfaces of the fitting or part thereof.

[0011] Although tube fittings can be made from a wide variety of different metals, fittings of particular interest are made from steels containing 5 to 50, preferably 10 to 40, wt.% Ni. Preferred alloys contain 10 to 40 wt.% Ni and 10 to 35 wt.% Cr. More preferred are the stainless steels, especially the AISI 300 and 400 series steels. Of special interest are AISI 316, 316L, 317, 317L and 304 stainless steels, alloy 600, alloy C-276 and alloy 20 Cb, to name a few examples. Fittings made from such steels, and particularly from austenitic stainless steels, find particular use in high purity piping systems, i.e., piping systems used for processing high purity liquids and gases. *See*, the above-noted U.S. Patent No. 6,547,888 B1.

Low Temperature Carburized Stainless Steel

[0012] Case hardening is a widely used industrial process for enhancing the surface hardness of metal articles. In a typical commercial process, the workpiece is contacted with a carburizing gas at 1700° F (950° C) or above whereby carbon atoms diffuse into the article's surface. Hardening occurs through the formation of "carbide precipitates," i.e., specific metal carbide compounds arranged in the form of discrete particles separate and apart from the metal matrix in which they are contained.

[0013] Stainless steel is rarely case hardened by conventional gas carburization, because the carbide precipitates produced promote corrosion.

[0014] To overcome this problem, a technique was developed for case hardening stainless steel in which the workpiece is contacted with a carburizing gas below 1000° F. At these temperatures, and provided that carburization does not last too long, carbon

atoms diffuse into the workpiece surfaces with little or no formation of corrosion-promoting carbide precipitates. As a result, the workpiece surface not only becomes hardened but also the inherent corrosion resistance of the stainless steel is maintained or even improved.

[0015] Low temperature carburization produces a substantial amount of soot as an unwanted by-product. Normally, the amount of soot produced exceeds the amount of carbon taken up by the workpiece. Indeed, when the parts being carburized are small, such as in the case of ferrules or the like, the amount of soot created is often large enough to completely engulf adjacent parts, thereby forming an amalgamated mass of soot and carburized parts. In normal practice, this unwanted soot by-product is almost always removed from the workpiece such as by washing or the like prior to use.

[0016] In addition to soot, low temperature carburization also produces a heavy oxide film, at least when carbon monoxide is used as the carbon source. This heavy oxide film, which typically has a color ranging from light gold to dark gold-brown, is considerably different from the coherent chromium oxide film which makes stainless steel corrosion-resistant in that it is thicker and not coherent; i.e., the heavy oxide film is relatively porous. Therefore, this film is also removed before use to uncover the workpiece's carburized surface, thereby producing a "surface-cleaned" carburized workpiece. *See*, commonly assigned WO 02/063195 A (22188/06303), the disclosure of which is also incorporated herein by reference.

[0017] In practice, removing the heavy oxide film may be done mechanically. However, it is most often done by anodic electropolishing in which the workpiece is immersed in an aqueous acidic bath and subjected to a direct electrical current to cause oxidation and dissolution of the outermost metal surface layer of the workpiece and removal of the heavy oxide film attached thereto. *See*, for example, U.S. Patent No. 4,026,737, U.S. Patent No. 4,269,633, U.S. Patent No. 4,859,287 and U.S. Patent No. 4,620,882, which disclose similar electropolishing treatments used to clean native stainless steels in preparation for coloring by conventional stainless steel electrolysis coloring processes. The disclosures of these patents are also incorporated herein by reference,

[0018] Electropolishing of native stainless steels is normally done to remove a substantial proportion and preferably all of the so-called "Bilby layer," which is the surface layer of the native stainless steel containing contaminants as well as fracture grains. This layer is about 2.5 microns thick, and so electropolishing here is normally accomplished to remove at least this 2.5 micron surface layer and perhaps more.

[0019] In contrast, electropolishing low temperature carburized stainless steel is carried out to remove a minimum amount of the workpiece's metal surface, only about 1 micron or so. This is because the hardened "case" produced by low temperature carburization only extends down to the first 10-25 microns or so of the workpiece's surface and, moreover, most of the diffused carbon which forms this hardened case is located at or near the workpiece's outer surface. Therefore electropolishing of low temperature carburized stainless steel is normally carried out to remove only a minimum amount of the workpiece's metal surface, so that the carburized surface layer of the workpiece is left largely intact. For the same reason, electropolishing is preferred over other techniques for removing this heavy oxide layer such as mechanical polishing or the like, since electropolishing avoids removing too much of the workpiece's surface layer.

[0020] Once the heavy oxide film is removed, the low temperature carburized workpiece is ready for use as is. Alternatively, the workpiece can be subjected to still additional, optional processing steps.

Alternating Current Electrolysis Coloring

[0021] In accordance with the invention, a low temperature carburized stainless steel workpiece which has been electropolished for removing the heavy oxide film formed during low temperature carburization is colored by subjecting the workpiece to alternating current electrolysis in an electrolysis bath which contains a metal having multiple valence states and which is maintained at a neutral to slightly basic pH.

[0022] Coloring stainless steel by alternating current electrolysis is already known and shown, for example, in the above-noted U.S. Patent No. 4,859,287. As described there, an alternating current is applied to the stainless steel workpiece to be colored in such a way that the polarity of the electricity applied to the workpiece alters between positive and negative. The same approach is used in this invention except that, in the

inventive process, a neutral to mildly basic electrolysis bath is used. In addition, cycle times are typically longer. Moreover, activation of the workpiece's surface by treatment with nitric, phosphoric or other acid, with or without accompanying anodic or cathodic treatment, which is an important feature of known stainless steel coloring processes, is unnecessary with this invention.

[0023] The workpiece can take a wide variety of different forms. For example, the workpiece may be a fitting component, including but not limited to a fitting body, a nut, a ferrule, a gripping ring, etc. One commercially available and highly successful fitting is illustrated in FIGS. 1 and 1A. FIGS. 1 and 1A, which taken from U.S. Patent No. 6,629,708, the disclosure of which is incorporated herein by reference in its entirety. The workpiece may be any one or more of the components of the fitting illustrated by FIGS. 1 and 1A. The workpiece is not limited to the components of the fitting shown in FIGS 1 and 1A and may be a component of any type of fitting or a stainless steel part of any type of assembly.

[0024] FIG. 1 shows the fitting components in a finger tight position preparatory to final tightening, whereas FIG. 1A shows the fitting after final tightening. As shown, the fitting comprises a body 10 having a cylindrical opening 12 counterbored for receiving tube end 13. A tapered, frusto-conical camming mouth 14 is located at the axial outer end of the counterbore. A front ferrule 16 having a smooth, cylindrical inner wall 18 is closely received on the tube. The front ferrule has a frusto-conical outer surface 20 to be received in the camming mouth.

[0025] Associated with the front ferrule 16 and located axially outward therefrom is a rear ferrule 22 configured as shown with a tapered nose portion 24 and a rear flange 26 having an inclined end surface 28. The inclined end surface of the rear ferrule 22 provides a radial component as well as an axial component of the pull-up forces acting on the end surface as will be apparent to those skilled in the art. The tapered nose 24 enters a tapered camming surface in the rear surface of the front ferrule.

[0026] The ferrules 16, 22 are enclosed by a drive nut member 30 threaded to the body 10. During tightening and make-up of the fitting, the inner end face, flange, or shoulder 32 of the nut acts against the rear wall end surface 28 of the rear ferrule to drive the ferrules forwardly into the fully engaged position shown in FIG. 1A.

(i) Electrolysis Bath

[0027] The electrolysis bath used for the inventive coloring process contains ions of a metal having multiple valence states such as chromium, molybdenum, tungsten, manganese and vanadium. Specific examples of such ions include chromates, molybdates, tungstates, manganates and vanadates, for example, Cr^{+6} , CrO_4^{-2} , MoO_3^{-2} , MnO_4^{-2} , V^{+5} , VO_3^- (metavanadate), $\text{V}_2\text{O}_7^{-4}$ (pyrovanadate), and VO^{-4} (orthovanadate). Mixtures of these ions can also be used. Specific compounds which can be used to supply such ions include, but are not limited to, ammonium dichromate, ammonium molybdate, ammonium metatungstate, lithium molybdate, sodium molybdate, sodium vanadate, sodium manganate and the like.

[0028] The concentration of the multivalent metal ion can vary widely, and any concentration can be used which will give the desired result. In general, concentrations ranging from about 0.01 to 1.0 moles/liter, more typically about 0.05 to 0.5 moles/liter, or even about 0.1 to 0.3 moles/liter, have been found to be useful.

[0029] The pH of the electrolysis bath used in the inventive process is normally maintained between about 5-12, more typically about 6-11 or even 7-10. This represents a significant departure from prior electrolytic processes for coloring stainless steel in which the electrolysis baths are maintained at strongly acidic or strongly basic pH's through the addition of strong acids such as sulfuric acid or nitric acid, or strong bases such as sodium hydroxide. Such pH adjusters are not normally used in the electrolysis baths of the present invention and, indeed, are preferably avoided.

(ii) Alternating Electric Current

[0030] In accordance with the invention, an electropolished low temperature carburized stainless steel workpiece is colorized by subjecting the workpiece to alternating current electrolysis in an electrolysis bath as described above. This is done by alternating the polarity of the electrical current applied to the workpiece in a similar manner to that described in the above-noted U.S. Patent No. 4,859,287. Preferably this is done so that a plot of current density versus time assumes a generally rectangular wave form. Most preferably, this is done so that equal amounts of electrical current are applied in both parts of each cycle as illustrated, for example, in the waveform of Fig. 2 of this disclosure. In this context, "equal" means that the absolute amount of electrical

current applied per unit of surface area of the part being colorized in the positive pulse of each cycle, as determined by integrating its current density/time waveform, is equal to the absolute amount of electrical current applied per unit of surface area in the negative pulse of each cycle.

[0031] This is most easily done by regulating the positive and negative pulse of each cycle to have the same magnitude and duration, as illustrated in Fig. 2. For example, if the amplitude of a positive pulse is +1 Amp and its duration is 100 milliseconds, the amplitude of the negative pulse of the same cycle should also be - 1 Amp and its duration should also be 100 milliseconds. Alternatively, the magnitudes and durations of the positive and negative pulses can be different, so long as the total amount of current supplied per unit of area is essentially the same in the positive and negative pulses.

[0032] The magnitude and duration of the applied electrical current varies depending on the composition of the electrolysis bath and can easily be determined by routine experimentation in light of the working examples presented below. In general, the magnitude of the applied current, in terms of current density, should generally be between about 0.01 to 3 A/in². This means that the current density in each positive pulse should be between about +0.01 and +3 A /in², while the current density in each negative pulse should be between about -0.01 and -3 /in². More typically, the magnitude of the applied current will be between about 0.02 to 1 A/in² or even about 0.03 to 0.7 A/in². Similarly, the duration of each pulse should normally be about 15-1000 milliseconds, more commonly about 50-500 milliseconds, or even 75-200 milliseconds. Pulses lasting about 100 milliseconds have been found to be especially convenient, although pulses lasting less than 15 and more than 1000 milliseconds can also be used.

[0033] As indicated above, the most convenient way of carrying out alternating current electrolysis in accordance with the invention is to adopt the wave form illustrated in Fig. 2 in which alternating pulses of positive and negative current of equal current densities and equal durations are applied to the workpiece immediately following one another. Thus, Fig. 2 shows that the duration 12 of positive pulse 14 is equal to the duration 16 of negative pulse 18, the magnitude 20 of positive pulse 14 is

equal to the magnitude 22 of negative pulse 18, and no delay is inserted between adjacent positive and negative pulses.

[0034] Other approaches, however, can also be used. For example, a delay (where the workpiece is held at zero potential) can be inserted between successive positive and negative pulses. In addition, the magnitude and duration of the positive and negative pulses can be varied from cycle to cycle. Similarly, the magnitude and duration of the positive pulse can be different from the magnitude and duration of the negative pulse in a particular cycle, provided that the absolute amounts of electrical current supplied in both pulses is essentially equal, as indicated above. Finally, additional positive and negative pulses can be included in the pattern of electrical current provided as described in col. 9, lines 9-28 of the above-noted U.S. Patent No. 4,859,287, so long as the last applied electric current is an alternating current or negative pulse current as described there.

[0035] Finally, it should be appreciated that the different approaches described above can be applied over the entire course of treatment of the workpiece or, alternatively, over only a portion of this treatment.

WORKING EXAMPLES

[0036] In order to describe the invention more thoroughly, the following working examples were conducted.

Examples 1-10

[0037] In these examples, stainless steel ferrules made from AISI 316 stainless steel were low temperature carburized in general accordance with the above-noted U.S. Patent No. 6,547,888 B1. After washing to remove the soot produced during carburization, the ferrules were electropolished to remove the heavy oxide coating that had also formed during carburization. The electropolished ferrules were then tumbled for 8 minutes in the presence of detergents, burnishing compounds and tumbling media for enhancing surface smoothness and then rinsed with water and dried, thereby producing electropolished ferrules each having a surface area of about 0.63 in².

[0038] The electropolished ferrules so obtained were then colorized by an electrolytic coloring process in accordance with the invention. This was done by subjecting the ferrules, which were mounted on a titanium anode, to alternating current electrolysis using an aqueous electrolysis bath containing 0.15M Na_2MoO_4 . The pH of the electrolysis bath was approximately 9.5, which was due solely to the Na_2MoO_4 , no additional acid or base being present. Electrolysis was carried out using alternating pulses of positive and negative current, each pulse lasting 100 milliseconds with no delays between the pulses. Ten different experiments were conducted at different current densities ranging from 0.033-0.13 A/in^2 . Each experiment lasted about 22 minutes, with the color of the ferrules obtained being monitored and recorded each minute.

[0039] The current densities employed, and the results obtained, are set forth in the following Table 1. In this table, the following abbreviations are used:

G = Gold

B = Blue

DG = Dark Gold

T1 = Transition No. 1 constituting a reddish/blue rainbow effect

T2 = Transition No. 2 constituting a greenish/gold rainbow effect

T3 = Transition No. 3 constituting a bluish/gold rainbow effect

Table 1
Color of Treated Ferrules as a Function of Current Density and Time

<u>Ex</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Current Density A/in ²	0.033	0.044	0.055	0.066	0.077	0.088	0.099	0.11	0.12	0.13
1 min	G	G	G	G	G	G	B	B	B	B
2 min	G	G	G	T1	B	B	B	B	B	T3
3 min	G	G	T1	T1	B	B	B	T3	G	G
4 min	G	G	T1	B	B	T3	T3	G	G	G
5 min	T	T1	T1	B	B	T3	T3	G	G	G
6 min	T	T1	B	B	T3	T3	T3	G	G	DG
7 min	T	T1	B	B	T3	G	G	G	G	DG
8 min	T	T1	B	B	T3	G	G	G	G	DG
9 min	T	T1	B	B	G	G	G	G	DG	DG
10 min	T	T1	B	B	G	G	G	G	DG	DG
11 min	T	B	B	G	G	G	G	G	DG	DG
12 min	B	B	T2	G	G	G	G	G	DG	DG
13 min	B	B	T2	G	G	G	G	G	DG	DG
14 min	B	B	T2	G	G	G	G	G	DG	DG
15 min	B	B	T2	G	G	G	G	G	DG	DG
16 min	B	B	T2	G	G	G	G	G	DG	DG
17 min	B	B	T2	G	G	G	G	G	DG	DG
18 min	B	B	T2	G	G	G	G	G	DG	DG
19 min	B	B	T2	G	G	G	G	G	DG	DG
20 min	B	T2	T2	G	G	G	G	G	DG	DG
21 min	B	T2	T2	G	G	G	G	G	DG	DG
22 min	B	T2	T2	G	G	G	G	G	DG	DG

[0040] From Table 1, it can be seen that significantly different colors, specifically blue, gold and dark gold, can be imparted to low temperature carburized stainless steel articles by the technology of the present invention.

Examples 11-13

[0041] Examples 1-10 were repeated, except that the current densities ranged from 0.44-0.64 A/in². The results obtained are set forth in the following Table 2. "GR" in this table refers to the color green.

Table 2
Color of Treated Ferrules as a Function of Current Density and Time

<u>Ex</u>	<u>11</u>	<u>12</u>	<u>13</u>
Current Density A/in ²	0.44	0.055	0.64
60 sec	GR	GR	GR
65 sec	GR	GR	GR
70 sec	GR	GR	GR

[0042] From Table 2, it can be seen that still another significantly different color, specifically green, can be imparted to low temperature carburized stainless steel articles by the technology of the present invention.

Examples 14 and 15

[0043] Examples 1-13 were repeated, except that the current densities ranged from 0.44-0.55 A/in² while total treatment times ranged from 7 to 10 minutes. The results obtained are set forth in the following Table 2. "R" in this table refers to the color red.

Table 3
Color of Treated Ferrules as a Function of Current Density and Time

<u>Ex</u>	<u>14</u>	<u>15</u>
Current Density A/in ²	0.44-0.49	0.055
7 min	R	R
8 min	R	R
9 min	R	R
10 min	R	R

[0044] From Table 3, it can be seen that still another significantly different color, specifically red, can be imparted to low temperature carburized stainless steel articles by the technology of the present invention.

Examples 16-25

[0045] Examples 1-10 were repeated, except that the electrolysis solution was composed of 0.2M (NH₄)₆Mo₇O₂₄·4H₂O. The results obtained are set forth in the following Table 4. In this table, the following additional abbreviations are used:

PR = Pinkish Red

T4 = Transition No. 4 constituting a gold/pinkish red rainbow effect

T5 = Transition No. 5 constituting a pinkish red /green rainbow effect

Table 4
Color of Treated Ferrules as a Function of Current Density and Time

Ex	16	17	18	19	20	21	22	23	24	25
Current Density A/in ²	0.033	0.044	0.055	0.066	0.077	0.088	0.099	0.11	0.12	0.13
1 min	G	G	G	G	G	B	B	B	B	B
2 min	G	G	G	G	T3	B	B	T3	T3	G
3 min	G	G	T3	T3	B	T3	T3	G	G	G
4 min	G	G	T3	B	B	G	T3	G	G	G
5 min	G	T3	B	B	B	G	G	G	T4	PR
6 min	G	B	B	B	B	G	G	T4	PR	PR
7 min	G	B	B	B	B	G	G	PR	PR	PR
8 min	T3	B	B	B	B	T4	T4	PR	PR	PR
9 min	T3	B	B	B	B	PR	PR	PR	PR	GR
10 min	T3	B	B	B	B	PR	PR	PR	T5	GR
11 min	T	B	B	B	B	PR	T5	PR	T5	T2
12 min	B	B	B	B	T3	PR	GR	PR	T5	G
13 min	B	B	B	B	T3	PR	GR	T5	T5	G
14 min	B	B	B	T3	T3	PR	GR	T5	T5	G
15 min	B	B	T3	T3	G	PR	GR	T5	T5	G
16 min	B	B	T3	G	G	PR	GR	GR	T5	G
17 min	B	T3	G	G	G	T5	GR	GR	GR	DG
18 min	B	T3	G	G	G	T5	GR	GR	T2	DG
19 min	B	G	G	G	G	GR	GR	GR	T2	
20 min	B	G	G	G	T4	GR	T2	T2	G	
21 min	B	G	G	G	PR	GR	T2	G		
22 min	T3	G	G	G	PR	GR	T2			

[0046] From Table 4, it can be seen that other multivalent metal salts can also be used to impart significantly different colors, specifically blue, gold and dark gold, green and pinkish red, to low temperature carburized stainless steel articles by the technology of the present invention.

Examples 26-29

[0047] Examples 1-10 were repeated, except that the electrolysis baths were composed of different multivalent metal salts, no additional acids or bases being added. In addition, current densities were also varied. The conditions and results obtained are

set forth in the following Table 5. In this table, the following additional abbreviations are used:

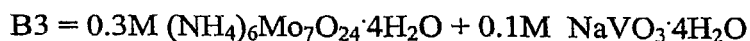
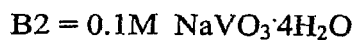
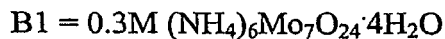


Table 5
Color of Treated Ferrules as a Function of Current Density and Time

<u>Ex</u>	<u>26</u>	<u>27</u>	<u>28</u>
Current Density A/in ²	0.033	0.044	0.055
Electrolysis bath	B1	B2	B3
2 min	Blue	Yellow	
5 min	Yellow	Blue	Orange
10 min	Gold	Blue	Orange
15 min	Red	Light Blue	Chartreuse
20 min	Orange	Blue	Chartreuse
25 min	Light Green	Blue	Green
30 min	Yellow	Chartreuse	Yellow
40 min	Gold	Yellow	

[0048] From Table 5, it can be seen that various different multivalent metal salts, including mixtures of such salts, can also be used to impart significantly different colors to low temperature carburized stainless steel articles by the technology of the present invention.

Comparative Example A

[0049] Examples 26-28 were repeated, except that the current density was 0.066 A/in² and the electrolysis bath was composed of 0.5M NaNO₃. The results obtained are set forth in the following Table 6:

Table 6
Color of Treated Ferrules as a Function of Current Density and Time

<u>Ex</u>	<u>Comp A</u>
Current Density A/in ²	0.066
Electrolysis bath	0.5M NaNO ₃
2 min	Blue
5 min	Yellow
10 min	Gold
15 min	Gold
20 min	Light Brown
25 min	Light Blue
30 min	Light Brown

[0050] From Table 6, it can be seen that different colors can be imparted to low temperature carburized stainless steel articles electrolytically even if the electrolysis bath does not contain a metal having multiple valence states. However, the electrolysis bath depleted rapidly requiring frequent replenishing, which is disadvantageous from a processing standpoint. Moreover, the colors obtained were not uniform, which is commercially unattractive.

[0051] Although only a few embodiments of the present invention have been described above, it should be appreciated that all such modifications can be made without departing from the spirit and scope of the invention. All such modifications are intended to be included within the scope of the present invention, which is to be limited only by the following claims:

Claims:

1. A process for coloring a surface-cleaned low temperature carburized stainless steel workpiece comprising subjecting the workpiece to alternating current electrolysis in an electrolysis bath containing a metal having multiple valence states and having a neutral to slightly basic pH.
2. The process of claim 1, wherein the low temperature carburized stainless steel workpiece is surface-cleaned by electropolishing.
3. The process of claim 1 wherein the pH is about 7-10.
4. The process of claim 1, wherein the metal having multiple valence states is chromium, molybdenum, tungsten, manganese, vanadium, or a mixture thereof.
5. The process of claim 4, wherein the electrolysis bath contains a chromate, molybdate, tungstate, manganate, vanadate or mixture thereof.
6. The process of claim 1, wherein the alternating electrical current defines cycles, each cycle having a positive pulse and a negative pulse, and further wherein the absolute value of the amounts of electrical current applied to the workpiece, in terms of current density, in the positive and negative pulses of each cycle are essentially equal.
7. The process of claim 6, wherein the duration of the positive pulse and the duration of the negative pulse of each cycle are essentially the same, and further wherein the magnitude of the electrical current applied to the workpiece, in terms of current density, in the positive and negative pulses of each cycle are essentially the same.
8. The process of claim 7, wherein the duration of each pulse is about 15-1000 milliseconds, and further wherein the current density of each pulse is about 0.01 to 2 A/in².
9. The process of claim 8, wherein the duration of each pulse is about 75-200 milliseconds, and further wherein the current density of each pulse is about 0.03 to 0.7 A/in².

10. The process of claim 6, wherein during at least a portion of the electrolysis treatment, the waveform of the electrical current applied to the workpiece includes a delay between successive positive and negative pulses.

11. The process of claim 6, wherein during the entire electrolysis treatment, the magnitude and duration of the positive and negative pulses of each cycle of alternating current are essentially the same.

12. The process of claim 6, wherein during at least a portion of the electrolysis treatment, the magnitude and duration of the positive and negative pulses of the alternating current are varied from cycle to cycle.

13. The process of claim 6, wherein during at least a portion of the electrolysis treatment, the magnitude and duration of the positive pulse of each cycle is different from the magnitude and duration of the negative pulse in a particular cycle.

14. The process of claim 6, wherein during at least a portion of the electrolysis treatment, additional positive and negative pulses are included in the pattern of electrical current provided to the workpiece.

15. The process of claim 1, wherein the electrolysis bath contains at least one of sodium molybdate, ammonium molybdate, sodium vanadate and sodium nitrate, and wherein the pH of the electrolysis bath is between about 7 and 10.

16. The process of claim 15, wherein the electrolysis bath contains no added acid or base.

17. A low temperature carburized stainless steel workpiece having an electrolytic coating exhibiting a uniform color selected from the group consisting of blue, green, red, pinkish-red, yellow, gold, light brown, orange, chartreuse and light green.

18. The workpiece of claim 17, wherein the workpiece is a tube fitting.

19. The workpiece of claim 18, wherein the workpiece is a ferrule.