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(71) Applicant: **FABBRICA D'ARMI PIETRO BERETTA
S.p.A.
25122 Brescia (IT)**

(72) Inventor: **Gussalli Beretta, Ugo
25063 Gardone Val Trompia (Brescia) (IT)**

(74) Representative: **Coppo, Alessandro
Ing. Barzanò & Zanardo Milano S.p.A.,
Via Borgonuovo, 10
20121 Milano (IT)**

(54) **Process for providing a tortoise-shell chromatic effect to metallic substrates**

(57) The present invention relates to a chemical process for providing a tortoise-shell chromatic effect to nickelated metallic substrates, which comprises heating the metallic substrate to 100-110°C and subsequent

buffering at a temperature of 40-110°C with an oxidizing solution based on sodium thiosulfate, a reagent metal and an acidifying compound.

EP 1 336 669 A2

Description

[0001] The present invention relates to a process for providing a tortoise-shell chromatic effect to metallic substrates.

[0002] In particular, the present invention relates to a process for providing a tortoise-shell chromatic effect to nickelated components of fire-arms.

[0003] It is known that the so-called tortoise-shell effect is a particular spotted chromatic effect conferred for ornamental purposes to tools or metallic parts of devices of varying origins.

[0004] In the fire-arm industry, the tortoise-shell effect is particularly requested for providing an aesthetically pleasant chromatic effect to the action body or other metallic parts of shotguns.

[0005] A tortoisng process of metallic substrates which requires high operating temperatures and also a low temperature chemical process capable of providing a simple uniform colouring to metallic substrates, are currently known.

[0006] The high temperature tortoisng process consists in the thermal treatment of a steel matrix which comprises heating to a temperature of about 700°C and quenching the steel in an aqueous solution of oxidizing salts.

[0007] The spotted colouring is created by the different surface oxidation degree of the steel and by the different thickness of the oxide layer formed.

[0008] This tortoisng process of the known art, however, is not without its drawbacks which can mainly be attributed to the distortion of the metallic materials due to the considerable thermal stress to which they are subjected during the quenching operation.

[0009] The more reduced the dimensional tolerances of the metallic articles or components treated, the greater this problem becomes.

[0010] In the case of the treatment of metallic components for high-precision articles, in fact, even a limited distortion or almost imperceptible deformation of the component can jeopardize its adequacy for the end-use.

[0011] In the tortoisng processes of gun action bodies, for example, it has been found that even minimum structural distortions can make them unusable.

[0012] Furthermore, the thermal treatment required for obtaining the particular aesthetic tortoise-shell effect has a negative influence on the hardness and mechanical performance in general of the metallic component treated.

[0013] Viceversa, chemical colouring processes of metals at a low temperature not only have the disadvantage of not being suitable for providing a spotted chromatic effect on the metals but also have the additional drawback that the chromatic layer produced can be easily removed by simple scratching.

[0014] With the tortoisng techniques currently available, it is consequently not possible to obtain a tortoise-shell chromatic effect which persists with time, is resist-

ant to scratching and does not produce significant distortions of the metallic end-products treated.

[0015] The Applicant has now identified a chemical tortoisng process which is effected at non-high temperatures and which consequently considerably limits the occurrence of the drawbacks described above.

[0016] One of the main objectives of the present invention therefore relates to providing a process for giving a tortoise-shell chromatic effect to metallic substrates without having to resort to temperatures which cause distortion of the metals treated.

[0017] Another objective of the present invention relates to a chemical tortoisng process of end-products or metallic components which allows the production of a long-lasting chromatic effect, which is appreciable from an aesthetic point of view.

[0018] A further objective of the present invention relates to a chemical process capable of providing, at non-high temperatures, a persistent tortoise-shell chromatic effect to nickelated components of fire-arms.

[0019] In view of the above objectives and others which will become evident from the following description, a first aspect of the present invention relates to a process for providing a tortoise-shell chromatic effect to substrates which includes the heating of a metallic substrate and application, under heat, on a portion of said metallic substrate, of an oxidizing solution comprising a thiosulfate, a reagent metal and an acidifying compound.

[0020] In the process of the invention, the metallic substrate to be treated is heated to a temperature at which there are substantially no thermal distortions which can jeopardize its use in high-precision applications.

[0021] The oxidizing solution of the invention is typically a solution based on sodium thiosulfate containing a reagent metal conveniently in the form of an acetate, preferably consisting of copper or lead acetate or their mixtures.

[0022] Within the scope of the present invention, the term acidifying compound includes compounds with acid hydrolysis or however compounds which when added to an aqueous solution are capable of reducing its pH.

[0023] Suitable acidifying compounds comprise organic acids such as carboxylic acids, for example, acetic acid, citric acid; oxalic acid, and potassium acid tartrate; inorganic acids such as hypophosphorous acid; salicylic acid; ketones such as acetone; aldehydes such as formic aldehyde and acetic aldehyde and their mixtures.

[0024] Substrates suitable for being subjected to the tortoisng process of the invention comprise metallic and non-metallic matrixes, provided they have at least one surface portion with a metallic layer, galvanically deposited or with another technology. Plastic matrixes with a nickelated surface, steel matrixes, nickelated steels, metal alloys such as aluminum, copper, nickel alloys and super-alloys, can be used, for example.

[0025] Nickelated details or components of end-prod-

ucts and articles for varying uses, with particular reference to nickelated details for fire-arms, such as gun action bodies, can be appropriately treated with the process of the invention.

[0026] The application of said oxidizing solution advantageously takes place by means of buffering on localized portions of the metallic substrate to be treated so as to cause oxidation and consequently a chromatic variation, limited to the buffered areas. In the areas buffered with the oxidizing solution, the surface metal layer undergoes a more intense oxidation process the greater the residence time of the oxidizing solution.

[0027] An embodiment of the process of the invention comprises the direct development of the chromatic effect on the metallic substrate using a solution based on thiosulfate containing copper acetate as reagent metal.

[0028] In accordance with this embodiment, a metallic substrate is heated to a temperature conveniently within the range of 100 to 110°C and subsequently buffered with a chromatically effective quantity of an aqueous solution containing sodium thiosulfate, copper acetate and potassium acid tartrate, at a temperature advantageously within the range of 40-110°C, preferably 60-80°C, until the development of the desired chromatic variation. The buffering phase can be repeated once or several times, until the desired tonality or chromatic effect is obtained.

[0029] It has been found that under these conditions, the tortoise-shell chromatic effect is caused by the oxidizing action of the solution on the surface of the metallic substrate. The coloured oxidized layer formed is firmly anchored to the metallic surface producing a long-lasting chromatic effect.

[0030] The Applicant has discovered that the direct development of a long-lasting chromatic variation which is particularly appreciable from an aesthetic point of view, is obtained using an oxidizing aqueous solution containing 220-240 g/l of sodium thiosulfate, 30-40 g/l of copper acetate and 30-40 g/l of potassium acid tartrate.

[0031] According to another embodiment of the process of the invention, it is possible to obtain the formation of the tortoise-shell effect with a two-phase treatment. This further embodiment of the invention therefore includes:

a first treatment phase which comprises the heating of a metallic substrate to a temperature conveniently within the range of 140-150°C and the application of a chromatically effective quantity of an aqueous solution containing sodium thiosulfate, lead acetate and an acidifying component, preferably consisting of potassium acid tartrate and, without rinsing;
a second treatment phase which comprises the application of a second oxidizing solution to the substrate, conveniently brought to a temperature of 40-80°C, preferably 50-60°C. The application of said second oxidizing solution can be effected by

means of buffering or by the direct immersion therein of the metallic substrate.

[0032] This second oxidizing solution contains a strong oxidizing agent, preferably consisting of ammonium persulfate, preferably present in a quantity ranging from 150-180 g/l.

[0033] It has been found that the process of the invention allows a variety of chromatic effects and different colourings to be obtained, by simply increasing the contact time of the oxidizing solutions on the surface of the metallic substrates. It is thus possible to produce yellow-gold, red, blue and grey colourings and shades in different tonalities.

[0034] The following examples are provided for purely illustrative purposes of the present invention and should not be considered as limiting its protection scope which is clearly defined by the enclosed claims.

EXAMPLE 1

[0035] A nickelated steel action body for a shotgun was initially heated to a temperature of 100°C and subsequently subjected to localized buffering at a temperature of 70°C with an oxidizing aqueous solution containing 230 g/l of sodium thiosulfate, 35 g/l of copper acetate and 35 g/l of potassium acid tartrate, until a spotted colouring, of the tortoise-shell type, is formed.

EXAMPLE 2

[0036] An aqueous solution containing 230 g/l of sodium thiosulfate, 22 g/l of lead acetate and 25 g/l of potassium acid tartrate was applied with a buffer on a nickel alloy article heated to a temperature of 140°C. In a subsequent phase, the article was immersed or buffered, without rinsing, at a temperature of 60°C, with an aqueous solution containing 160 g/l of ammonium persulfate. After a few minutes, a chromatic variation, with a typical tortoise-shell effect, is formed in the buffered areas.

EXAMPLE 3

[0037] Oxidizing solutions suitable for use in the buffering phase of the tortoisng process of the invention:

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|------------------------|-------------|
| Sodium thiosulfate | 220/240 g/l |
| Copper or lead acetate | 25-40 g/l |
| Citric acid | 30-40 g/l |

| | |
|------------------------|------------------------|
| Sodium thiosulfate | 220/240 g/l |
| Copper or lead acetate | 25-40 g/l |
| Hypochlorous acid | 0.5 cc/l (d=1,23 g/cc) |

| | |
|------------------------|-------------|
| Sodium thiosulfate | 220/240 g/l |
| Copper or lead acetate | 25-40 g/l |
| Acetone | 40 ml/l |

| | |
|------------------------|-------------|
| Sodium thiosulfate | 220/240 g/l |
| Copper or lead acetate | 25-40 g/l |
| Formic aldehyde | 30 ml/l |

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|------------------------|-------------|
| Sodium thiosulfate | 220/240 g/l |
| Copper or lead acetate | 25-40 g/l |
| Acetic aldehyde | 20-30 ml/l |

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|------------------------|-------------|
| Sodium thiosulfate | 220/240 g/l |
| Copper or lead acetate | 25-40 g/l |
| Oxalic acid | 10-15 g/l |

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|------------------------|-------------|
| Sodium thiosulfate | 220/240 g/l |
| Copper or lead acetate | 25-40 g/l |
| Salicylic acid | 15-20 g/l |

| | |
|------------------------|-------------|
| Sodium thiosulfate | 220/240 g/l |
| Copper or lead acetate | 25-40 g/l |
| Acetic acid | 10 ml/l |

Claims

1. A process for providing a tortoise-shell chromatic effect to substrates which comprises heating of the substrate to a suitable temperature for providing a chromatic effect and the application under heat on a portion of said substrate of an oxidizing solution comprising a thiosulfate, a reagent metal and an acidifying compound.
2. The process according to claim 1, **characterized in that** said thiosulfate is sodium or potassium thiosulfate.
3. The process according to claim 1 or 2, **characterized in that** said metal is selected from copper acetate, lead acetate or their mixtures.
4. The process according to any of the claims 1-3, **characterized in that** said acidifying compound is selected from potassium acid tartrate, citric acid, hypophosphorous acid, acetone, formic aldehyde, acetic aldehyde, oxalic acid, salicylic acid, acetic acid and their mixtures.

5. The process according to any of the previous claims 1-4, **characterized in that** said oxidizing solution is applied by buffering on said substrate.

6. The process according to any of the previous claims 1-5, wherein there is the direct development of a tortoise-shell chromatic effect by heating said metallic substrate to a temperature within the range of 100-110°C and buffering at a temperature within the range of 40-110°C with an oxidizing solution comprising

| | |
|-------------------------|-------------|
| sodium thiosulfate | 220-240 g/l |
| copper acetate | 30-40 g/l |
| potassium acid tartrate | 30-40 g/l |

until the chromatic effect is obtained.

7. The process according to claim 6, **characterized in that** the buffering of the metallic substrate takes place at a temperature ranging from 60-80°C.

8. The process according to any of the previous claims 1-5, wherein a tortoise-shell chromatic effect is developed in two phases, said process comprising:

- an application phase by buffering a solution comprising

| | |
|-------------------------|-------------|
| sodium thiosulfate | 220-240 g/l |
| lead acetate | 30-40 g/l |
| potassium acid tartrate | 30-40 g/l |

on a metallic substrate heated to a temperature ranging from 140-150°C and

- a second application phase of a second oxidizing solution on said substrate at a temperature ranging from 40-80°C.

9. The process according to claim 8, **characterized in that** in said second phase, the application of the oxidizing solution takes place by buffering or by immersion of the metallic substrate.

10. The process according to claim 8 or 9, **characterized in that** said second oxidizing solution is a solution of ammonium persulfate.

11. The process according to any of the previous claims 1-10, **characterized in that** said substrate comprises a metal coating.

12. The process according to claim 11, **characterized in that** said coating metal is selected from nickel, nickel alloys, steels, nickelated steels, copper, super-alloys.

13. The process according to any of the previous claims 1-12, **characterized in that** said metallic substrate is an action body of a gun.

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