(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 336 669 B9**

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

Note: Bibliography reflects the latest situation

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see
Description Paragraph(s) 18-22

(48) Corrigendum issued on:
03.10.2007 Bulletin 2007/40

(45) Date of publication and mention of the grant of the patent:
28.03.2007 Bulletin 2007/13

(21) Application number: **03075332.1**

(22) Date of filing: **04.02.2003**

(51) Int Cl.:
C23C 22/48 *(2006.01)* ***C23C 22/58*** *(2006.01)*
C23C 22/50 *(2006.01)* ***C23C 22/52*** *(2006.01)*
C01B 17/64 *(2006.01)*

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

Verfahren zum Bereitstellen eines schildkrötenpanzerartigen Farbeffekts auf Metalloberflächen

Procédé de fournir un effet de coloration du type carapace de tortue sur des surfaces métalliques

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PT SE SI SK TR

(30) Priority: **15.02.2002 IT MI20020307**

(43) Date of publication of application:
20.08.2003 Bulletin 2003/34

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- **DATABASE WPI Section Ch, Week 198012 Derwent Publications Ltd., London, GB; Class M14, AN 1980-21680C XP002032465 & SU 673 667 A (SHAKHOVA G A), 15 July 1979 (1979-07-15)**

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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 tortoising 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 tortoising 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 tortoising 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 tortoising 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] FR-A-2 735 075 discloses a process for providing a coloring effect to substrates wherein the contact between the coloring solution and the substrate can be done by immersion at ambient temperature and wherein the coloring solution comprises sodium thiosulphate, lead or copper acetate and potassium acid tartrate.

[0015] GB-A-1 229 502 discloses a process for making designs on metal surfaces including a step of coating the colored metal surface with a heat and corrosion resistant transparent coating.

[0016] In the DATABASE WPI Section Ch, Week 198049 Derwent Publications Ltd, Class A35, AN 1980-88040C XP002032466 & SU 729281 A (LAKIZA W) 28 Capri1 1980, a process for providing colouring of metal surfaces by treatment with lead acetate, sodium hyposulphite at 15-80°C is disclosed.

[0017] WO 97/35046 discloses a process for providing a a cloring metallic effect to metallic substrates wherein the substrate is contacted with sodium hyposulfite lead and copper acetate by immersion at a temperature of 50 to 100°C.

[0018] With the tortoising techniques currently available, it is consequently not possible to obtain a tortoise-shell chromatic effect which persits with time, is resistant to scratching and does not produce significant distortions of the metallic end-products treated.

[0019] The Applicant has now identified a chemical tortoising process which is effected at non-high temperatures and which consequently considerably limits the occurence of the drawbacks described above.

[0020] 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.

[0021] Another objective of the present invention relates to a chemical tortoising 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.

[0022] 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.

[0023] 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 as claimed in the appended claims

[0024] In the process of the invention, the metallic substrate to be treated is heated to a suitable temperature for providing a chromatic effect, said temperature being a non-high temperature at which there are no thermal distortions caused in the substrate which can jeopardize its use in high-precision applications.

[0025] 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.

[0026] 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.

[0027] Suitable acidifying compounds comprise organic acids such as carboxylic acids, for example, acetic acid, citric acid; oxalic acid, salicylic acid and potassium acid tartrate; inorganic acids such as hypochlorous acid and hypophosphorous acid.

[0028] Substrates suitable for being subjected to the tortoising process of the invention comprise metallic matrixes, provided they have at least one surface portion with a metallic layer, galvanically deposited or with another technology. Steel matrixes, nickelated steels, metal alloys such as aluminum, copper, nickel alloys and superalloys, can be used, for example.

[0029] Nickelated details or components of end-products 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.

[0030] 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. process the greater the residence time of the oxidizing solution.

[0031] 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.

[0032] 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.

[0033] 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.

[0034] 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.

[0035] 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 an oxidizing solution to the substrate, conveniently brought to a temperature of 40-80°C, preferably 50-60°C. The application of said oxidizing solution can be effected by means of buffering or by the direct immersion wherein of the metallic substrate.

[0036] This oxidizing solution contains a strong oxidizing agent, preferably consisting of ammonium persulfate, preferably present in a quantity ranging from 150-180 g/l.

[0037] 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.

[0038] 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

[0039] 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

[0040] 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

[0041] Oxidizing solutions suitable for use in the buff-

ering phase of the tortoising process of the invention:

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
Oxalic acid	10-15 g/l

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 a metal coating of a substrate, which comprises:

   - heating the metallic substrate to a suitable temperature for providing a chromatic effect, said temperature being a non-high temperature at which there are no thermal distortions caused in the substrate,
   - application under heat, at a temperature within a range of 40 to 110°C, on a portion of said metallic substrate of an oxidizing solution comprising sodium or potassium thiosulfate, a reagent metal selected from cooper acetate and lead acetate and mixtures thereof, and an acidifying compound.

2. The process according to claim **characterized in that** said reagent metal is selected from copper acetate, lead acetate or their mixtures.

3. The process according to any of the claims 1-2, **characterized in that** said acidifying compound is selected from potassium acid tartrate, citric acid, hypophosphorous acid, oxalic acid, salicylic acid, acetic acid, hypochlorous acid and their mixtures.

4. The process according to any of the previous claims 1-34, **characterized in that** said oxidizing solution is applied by buffering on said metal coating of the substrate.

5. The process according to any of the previous claims 1-4, 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.

6. The process according to claim 5, **characterized in that** the buffering of the metallic substrate takes place at a temperature ranging from 60-80°C.

7. The process according to any of the previous claims 1-4, 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 an oxidizing solution on said substrate at a temperature ranging from 40-80°C.

8. The process according to claim 7, **characterized in that** in said second phase, the application of the oxidizing solution takes place by buffering or by immersion of the metallic substrate.

9. The process according to claim 7 or 8, **characterized in that** said second oxidizing solution is a solution of ammonium persulfate.

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

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

is an action body of a gun.

Patentansprüche

1. Verfahren zum Versehen einer Metallummantelung eines Substrats mit einem schildpattartigen Farbeffekt, wobei das Verfahren umfasst:

   Erhitzen des metallischen Substrats auf eine geeignete Temperatur zum Aufbringen eines Farbeffekts, wobei die Temperatur eine Nicht-Hochtemperatur ist, bei der keine thermischen Verwerfungen im Substrat bewirkt werden,
   Anwenden einer Oxidationslösung, die Natrium- oder Kaliumthiosulfat, ein aus Kupferazetat und Bleiazetat und Mischungen davon ausgewähltes Reagensmetall und eine säurebildende Verbindung aufweist, unter Wärme, bei einer Temperatur innerhalb eines Bereichs von 40 bis 110°C, auf einem Abschnitt des metallischen Substrats.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** das Reagensmetall aus Kupferazetat, Bleiazetat oder deren Mischungen ausgewählt wird.

3. Verfahren nach einem der Ansprüche 1 bis 2, **dadurch gekennzeichnet, dass** die säurebildende Verbindung aus Kaliumsäuretartrat, Zitronensäure, hypophosphoriger Säure, Oxalsäure, Salizylsäure, Essigsäure, unterchloriger Säure und deren Mischungen ausgewählt wird.

4. Verfahren nach einem der vorhergehenden Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** die Oxidationslösung durch Puffern auf der Metallummantelung des Substrats angewendet wird.

5. Verfahren nach einem der vorhergehenden Ansprüche 1 bis 4, wobei eine direkte Entwicklung eines schildpattartigen Farbeffekts durch Erhitzen des Metallsubstrats auf eine Temperatur innerhalb des Bereichs von 100-110°C und Puffern bei einer Temperatur innerhalb des Bereichs von 40-110°C mit einer Oxidationslösung stattfindet, die umfasst:

Natriumthiosulfat	220-240 g/l
Kupferazetat	30-40 g/l
Kaliumsäuretartrat	30-40 g/l

   bis der Farbeffekt erhalten wird.

6. Verfahren nach Anspruch 5, **dadurch gekennzeichnet, dass** das Puffern des Metallsubstrats bei einer Temperatur im Bereich von 60-80°C stattfindet.

7. Verfahren nach einem der vorhergehenden Ansprüche 1 bis 4, wobei ein schildpattartiger Farbeffekt in zwei Phasen entwickelt wird, das Verfahren umfassend:

   eine Anwendungsphase mittels Puffern einer Lösung, die

Natriumthiosulfat	220-240 g/l
Bleiazetat	30-40 g/l
Kaliumsäuretartrat	30-40 g/l

   aufweist, auf ein auf eine Temperatur im Bereich von 140-150°C erhitztes metallisches Substrat und
   eine zweite Anwendungsphase einer Oxidationslösung auf dem Substrat bei einer Temperatur im Bereich von 40-80°C.

8. Verfahren nach Anspruch 7, **dadurch gekennzeichnet, dass** in der zweiten Phase die Anwendung der Oxidationslösung mittels Puffern oder mittels Eintauchen des metallischen Substrats stattfindet.

9. Verfahren nach Anspruch 7 oder 8, **dadurch gekennzeichnet, dass** die Oxidationslösung eine Ammoniumpersulfatlösung ist.

10. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** das Ummantelungsmetall aus Nikkel, Nickellegierungen, Stählen, Nickelatstählen, Kupfer, Superlegierungen ausgewählt wird.

11. Verfahren nach einem der vorhergehenden Ansprüche 1 bis 10, **dadurch gekennzeichnet, dass** das metallische Substrat ein Aktionskörper einer Schusswaffe ist.

Revendications

1. Procédé pour fournir un effet de coloration du type carapace de tortue sur un revêtement métallique d'un substrat, qui comprend :

   - le chauffage du substrat métallique à une température adaptée afin de fournir un effet de coloration, ladite température étant une température non élevée à laquelle il n'y a pas de distorsion thermique causée dans le substrat,
   - l'application sous la chaleur, à une température dans une gamme de 40 à 110° C, sur une partie dudit substrat métallique d'une solution oxydante comprenant du thiosulfate de sodium ou de

potassium, un métal réactif sélectionné parmi l'acétate de cuivre et l'acétate de plomb et des mélanges de ceux-ci, et un composé acidifiant.

2. Procédé selon la revendication 1, **caractérisé en ce que** ledit métal réactif est sélectionné parmi l'acétate de cuivre, l'acétate de plomb ou leurs mélanges.

3. Procédé selon l'une quelconque des revendications 1 et 2, **caractérisé en ce que** ledit composé acidifiant est sélectionné parmi le tartrate d'acide de potassium, l'acide citrique, l'acide hypophosphoreux, l'acide oxalique, l'acide salicylique, l'acide acétique, l'acide hypochloreux et leurs mélanges.

4. Procédé selon l'une quelconque des revendications précédentes 1 à 3, **caractérisé en ce que** ladite solution oxydante est appliquée par tamponnage sur ledit revêtement métallique du substrat.

5. Procédé selon l'une quelconque des revendications précédentes 1 à 4, dans lequel il y a le développement direct d'un effet de coloration du type carapace de tortue par chauffage dudit substrat métallique à une température comprise dans une gamme de 100 à 110° C et tamponnage à une température comprise dans une gamme de 40 à 110° C avec une solution oxydante comprenant :

thiosulfate de sodium	220-240 g/l
acétate de cuivre	30-40 g/l
tartrate d'acide de potassium	30-40 g/l

jusqu'à obtention de l'effet de coloration.

6. Procédé selon la revendication 5, **caractérisé en ce que** le tamponnage du substrat métallique se produit à une température dans une gamme de 60 à 80° C.

7. Procédé selon l'une quelconque des revendications précédentes 1 à 4, dans lequel un effet de coloration du type carapace de tortue est développé en deux phases, ledit procédé comprenant .

- une phase d'application par tamponnage d'une solution comprenant :

thiosulfate de sodium	220-240 g/l
acétate de plomb	30-40 g/l
tartrate d'acide de potassium	30-40 g/l

sur un substrat métallique chauffé à une température comprise entre 140 et 150° C et
- une seconde phase d'application d'une solution oxydante sur ledit substrat à une température comprise entre 40 et 80° C.

8. Procédé selon la revendication 7, **caractérisé en ce que** dans ladite seconde phase, l'application de la solution oxydante se produit par tamponnage ou par immersion du substrat métallique.

9. Procédé selon la revendication 7 ou 8, **caractérisé en ce que** ladite solution oxydante est une solution de persulfate d'ammonium.

10. Procédé selon la revendication 1, **caractérisé en ce que** ledit métal de revêtement est sélectionné parmi le nickel, les alliages de nickels, les aciers, les aciers nickelés, le cuivre, les superalliages

11. Procédé selon l'une quelconque des revendications précédentes 1 à 10, **caractérisé en ce que** ledit substrat métallique est un corps d'action d'un pulvérisateur.

REFERENCES CITED IN THE DESCRIPTION

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