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(54) **Metallic coating and method to obtain the coating**

(57) The invention relates to a method for plating (electroplating or electroless plating) a metallic film coating onto a substrate, whereby the coating comprises fluorine containing particles, embedded in a metal matrix and distributed in a gradient throughout the thickness of the coating. The method comprises the steps of preparing a plating liquid and dispersing the fluorine containing particles therein, and subjecting the substrate to plating

in a plating bath under ultrasonic agitation, with the proviso that the power of ultrasonic agitation in the bath is changed during plating. The invention also relates to a product with a wear resistant and smooth surface, provided by a metallic coating obtained by the method, and in particular to a laundry iron with an improved soleplate.

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Description

FIELD OF THE INVENTION

5 **[0001]** The invention relates to a metallic coating, comprising particles, in particular fluorine containing particles, embedded in a metal matrix, and to a method to obtain the coating. The invention also relates to products with a wear resistant and smooth surface, provided by the metallic coating. The invention in particular relates to a laundry iron, comprising a soleplate with the metallic coating.

10 BACKGROUND OF THE INVENTION

[0002] A variety of materials has been proposed as laundry iron soleplate coating materials, including metal or inorganic materials, such as sol gel and enamel coatings, stainless steel, anodised and Cr/Ni layers. Also, organic polymer soleplate coating materials have been proposed, among which poly-tetra-fluoro-ethylene (PTFE) is most commonly used for low end and mid-end laundry irons. PTFE provides non-stick and low friction properties, which results in good gliding properties.

15 **[0003]** PTFE coatings, however, cannot meet some other important requirements for a good soleplate coating. PTFE coatings in particular suffer from poor scratch resistance and poor wear resistance. It has been proposed in US 6,138,389 therefore to improve the scratch properties by providing a metallic coating with fluorine bearing particles dispersed therein. Such a coating is provided onto the substrate by an electroplating method, whereby a plating liquid with therein dispersing fluorine containing particles is prepared, and the substrate is subjected to electroplating in an electroplating bath. The obtained coatings however exhibit a lower wear resistance than the pure metallic film coating, and the fluorine-bearing particles do not contribute to the gliding smoothness of the soleplate on an equal level as a pure PTFE coating.

20 **[0004]** Smooth gliding, wear resistance and stain resistance are among the most important properties of laundry irons. Improving these properties improves the convenience for the user and assures the iron to be smooth for a longer period as improved wear resistance prevents the coating from deterioration.

SUMMARY OF THE INVENTION

30 **[0005]** The present invention aims to provide a metallic coating, comprising fluorine containing particles embedded in a metal matrix, the coating having improved gliding, wear resistance and stain resistance over the prior art coating. The invention further aims to provide a method to obtain the coating, and to provide a product with an improved coating.

[0006] This aim is achieved according to the invention by a method for plating a metallic coating onto a substrate, whereby the coating comprises particles embedded in a metal matrix, the method comprising the steps of preparing a plating liquid and dispersing the particles therein, and subjecting the substrate to plating in a plating bath under agitation, with the proviso that the power of agitation in the bath is changed during plating. The method according to the invention provides a metallic coating on a substrate, whereby the coating comprises fluorine containing particles distributed in a gradient throughout the thickness of the coating. Such fluorine containing particle distribution has proven to be beneficial to the desired combination of smoothness, wear resistance and stain resistance of the coating. A distribution of particles over the thickness of the coating allows tailoring the properties of the coating according to where they are needed. It may well be that certain properties are needed close to a first interface, for instance the interface of coating and substrate, and that other properties are desired at a second interface, for instance the interface of coating and environment. The method according to the invention allows optimising the coating such that these needs can be fulfilled. Any plating method can be used in the method according to the invention, including electroplating and electroless plating, the latter being the preferred method. Particularly preferred is electroless nickel plating.

40 **[0007]** Although the advantages of the method according to the invention are particularly noticeable for a metallic coating comprising fluorine containing particles, it may in fact be used for a metallic coating comprising any type of dispersed particles, as long as it is desirable to obtain a particle distribution in the coating having a gradient throughout the thickness of the coating.

50 **[0008]** In a preferred embodiment of the method according to the invention the coating is plated onto a substrate by electroplating. Electroplating involves providing the substrate to be plated, as well as a piece of the metal to be plated on the substrate, and incorporating the substrate (usually as cathode) and the piece of metal (usually as anode) into an electrical circuit. The substrate and the piece of metal are immersed in a plating liquid, containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. According to the invention, the plating liquid also comprises particles dispersed therein, and preferably fluorine containing particles. A rectifier usually supplies a direct current to the anode, oxidizing the metal molecules that comprise it and allowing them to dissolve in the liquid. At the cathode, the dissolved metal ions in the plating liquid are reduced at the interface between the liquid and the cathode, such that they deposit onto the cathode. According to the method of the invention, the plating bath is agitated, preferably

ultrasonically, at least during part of the total plating process time, with the proviso that the power of ultrasonic agitation in the bath is changed during the plating. It has turned out that by changing the power of ultrasonic agitation in the plating bath, the concentration of particles migrating to the substrate can be influenced, such that a coating with a particle distribution having a gradient throughout the thickness is obtained.

5 [0009] In the method according to the present invention, any agitation method, such as stirring, may in principle be used. Suitable agitation methods involve mechanical stirring, such as screw stirring, magnetic stirring and/or ultrasonic agitation, the latter being the preferred agitation method.

[0010] Although the current flowing through the circuit may be changed during electroplating, preferably this current remains constant in the method according to the invention. Such an embodiment yields a more reliable and better controlled particle distribution throughout the thickness of the coating.

10 [0011] A further advantage of the method according to the invention is that the gradient plating can be accomplished with a limited amount of plating baths, and preferably with only one plating bath. This makes the method easy to realize at low operational cost.

15 [0012] In principle, the power of agitation in the bath can be changed according to any function in time, either continuously or discontinuously. In a preferred embodiment however, the method is **characterized in that** the power of agitation in the bath is changed during plating in a stepwise manner. The number of steps can be varied over a wide range, with a preferred range of between 1 and 20 separate steps, more preferred between 2 and 15, and most preferred between 3 and 10 separate steps.

20 [0013] It had advantages to characterize the method according to the invention in that the power of agitation is changed from a low level at the beginning of the plating time period to a high level at the end of the plating time period. More preferably, the power of agitation is changed from the low level to the high level in a monotonously increasing fashion. In an embodiment wherein fluorine containing particles are used, a coating is obtained having a relatively low amount of fluorine containing particles close to the substrate and an incrementally increasing amount of particles towards the outer surface of the coating. The relatively low amount of fluorine containing particles at the coating-substrate interface provides a coating with high hardness at this interface, and a good adhesion. The relatively high amount of fluorine containing particles at the coating-environment interface provides a coating with good gliding properties, as well as good stain resistance. The method of the invention can in principle be applied to any substrate including but not limited to steel substrates, stainless steel substrates, aluminium substrates, polymeric substrates, ceramic substrates, and so on.

25 [0014] The plating liquid into which the particles, and in particular the fluorine containing particles are dispersed can be any plating liquid known in the art. Ordinary electroplating liquids that can precipitate a metal at the cathode by an electroplating process or a non-electrolytic plating liquid that causes reduction precipitation by electrons supplied from the reducing agents may be used. Examples of suitable plating liquids include liquids of copper, nickel, chromium, zinc, cadmium, tin, iron, lead, precious metals and their alloys. If desirable, a surfactant can be used in the plating liquid of the present invention in order to finely disperse the fluorine containing particles in the plating liquid. Suitable surfactants include for instance water-soluble cationic surfactants, such as quaternary ammonium salts, secondary and tertiary

amines, imidazolines, and the like, non-ionic surfactants, such as polyoxyethylenes, polyethylene imines, esters, and the like and amphoteric surfactants. The amount of surfactant added to the plating liquid is typically from 0.001 to 0.1 % by weight of the weight of the fluorine containing particles.

40 [0015] The size of the particles dispersed in the electroplating liquid is not particularly limited. However, when the particle size is larger than the plated film coating thickness, the particles tend to come off from the plating surface by abrasion. Therefore, it is desirable to provide particles having a size smaller than the thickness of the plated film coating. The thickness of the plated film coating depends on the specific product to which the coating is applied. For a soleplate of a laundry iron for instance, coating thickness is preferably from 5 to 30 μm , more preferably from 10 to 20 μm . For a soleplate of a laundry iron therefore, preferred particle sizes are between 1 to 20 μm , more preferred between 3 and 15 μm .

45 [0016] The amount of particles within the plating liquid is determined by the desired amount of particle in the coating. A preferred method according to the invention is **characterized in that** the plating liquid comprises an amount of fluorine containing particles, sufficient to obtain between 0.5 - 80 vol.-% of fluorine containing particles, relative to the total volume of the metallic film coating. This relative amount of particles is usually sufficient to cover any desired variation in properties. Even more preferred is a method wherein the plating liquid comprises an amount of fluorine containing particles, sufficient to obtain between 10 - 50 vol.-% of fluorine containing particles, relative to the total volume of the metallic film coating.

50 [0017] The invention also relates to a product with a wear resistant and smooth surface, provided by a metallic coating obtainable by the method according to the invention, and to a product, provided with a metallic coating, comprising particles, embedded in a metal matrix, the particles being distributed in a gradient throughout the thickness of the coating. The metallic coating, obtainable by the method according to the invention is particularly useful when applied to the soleplate of a laundry iron. The metallic coating can be used continuously at high temperatures of up to at least 250°C and/or in hot water and/or in steam without permanent loss in physical properties or without turning brittle. Due to the

gradient of the fluorine-bearing particles in the coating (with preferably more particles towards the surface and less towards the substrate) the hardness and non-stick properties are improved where they are needed, and compared to the known coating, such as the one disclosed in US 6,138,389. Compared to metallic coatings containing uniformly distributed fluorine-bearing particles, the metallic film coating of the invention is harder close to the surface. On the one hand, this will improve the hardness and therefore also the scratch and wear resistance. On the other hand, there are more fluorine containing particles close to the surface on average, which improves the gliding smoothness of the coating.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The invention is illustrated by way of the following non-limitative examples, wherein:

Figure 1 shows a SEM graph of a cross section of a coating according to the invention, including a bar graph of the amount of fluorine through the thickness of the coating; and figure 2 shows the indentation hardness across a cross section of the coating of figure 1.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0019] It should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim. Use of the verb "comprise" and its conjugations does not exclude the presence of elements or steps other than those stated in a claim. The article "a" or "an" preceding an element does not exclude the presence of a plurality of such elements. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.

[0020] A Ni/PTFE coating was prepared by subjecting a substrate to electroless plating in a plating bath containing PTFE-particles under ultrasonic agitation. During the plating process, the power of ultrasonic agitation in the bath was changed in a stepwise fashion from close to zero W to about 150 W. With reference to figure 1, a SEM image of a cross-section of the electroless nickel coating 3 thus obtained is shown. Coating 3 is applied onto substrate 2. The amount of PTFE particles in the Ni matrix increases towards the outer surface 1 of the coating (the left side of the coating in figure 1). This effect is the result of the changing of the ultrasonic agitation power in the course of electroless plating. A SEM-EDX mapping analysis of the coating is also shown. The mapping was conducted to obtain the average amount of fluorine in 6 sections of the cross-section, denoted S1 to S6. The result shows that the closer to the surface 1 a section is taken of the EDX signals, the higher the fluorine (and thus the PTFE particle) content is. The concentration of fluorine and therefore of PTFE particles increases towards the outer surface 1 of the coating, away from the substrate 2.

[0021] Referring to figure 2, the indentation hardness level is shown for 24 sections of the coating. As shown by the dots in figure 2, section 1 is located at the interface between substrate 2 and coating 3, while section 24 is located at the coating surface 1. Sections 2 to 23 are located between the substrate 2 and the outer surface 1 of the coating 3, whereby a section n+1 is closer to the outer surface 1 than section n. The results show that the indentation hardness decreases when going from the substrate towards the surface of the coating. This is in line with the increasing amount of PTFE particles close to the surface of the coating. It also shows that the coating is harder close to the substrate and indeed even harder than coatings in which the fluorine particles are homogeneously distributed.

[0022] The gliding properties of the produced coating (Example I) were compared to the gliding properties of a Ni/PTFE coating, containing the same total amount of PTFE particles but homogeneously distributed through the thickness of the coating (Comparative Experiment A), and a Ni coating without PTFE particles (Comparative Experiment B). The gliding properties obtained on cotton and polyester fabrics were evaluated on a scale from 1 = poorest gliding performance to 5 = best gliding performance. The results are shown in Table 1 below, and demonstrate that a coating according to the invention has better gliding properties than both prior art coatings.

Table 1: Gliding properties

Coating	Comparative Exp. A		Example I		Comparative Exp. B	
	Cotton	Polyester	Cotton	Polyester	Cotton	Polyester
Gliding property	4.5	3.0	5.0	3.2-3.8	4.5	2.0

[0023] The metallic coating according to the invention can be used advantageously as a non-stick, wear resistant coating for domestic appliances, in particular for laundry irons.

[0024] It can also be particularly useful in other applications, including but not limited to coatings on bearing cages,

replacement of cadmium plating in threaded fasteners in airplane components, machinery components requiring corrosion protection and solid lubricity and moulds for IC transfer molding for instance. In all of these applications the coating according to the invention provides the desired self-lubricity and non-stick properties, while the gradient distribution of the PTFE particles through the thickness of the coating provides the desired adhesion of the coating to the substrate.

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Claims

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1. A method for plating a metallic coating onto a substrate, whereby the coating comprises particles, embedded in a metal matrix, the method comprising the steps of preparing a plating liquid and dispersing the particles therein and subjecting the substrate to plating in a plating bath under agitation, with the proviso that the power of agitation in the bath is changed during plating.

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2. Method according to claim 1, wherein the coating comprises fluorine containing particles.

3. Method according to claim 1 or 2, wherein the agitation comprises ultrasonic agitation.

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4. Method according to any one of the preceding claims, wherein the power of agitation in the bath is changed during plating in a stepwise manner.

3. Method according to claim 1 or 2, wherein the power of agitation is changed from a low level at the beginning of the plating to a high level at the end of the plating.

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4. Method according to claim 3, wherein the power of agitation is changed from the low level to the high level in a monotonously increasing fashion.

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5. Method according to any one of the preceding claims, wherein the plating liquid comprises an amount of fluorine containing particles, sufficient to obtain between 0.5 - 80 vol.-% of fluorine containing particles, relative to the total volume of the metallic film coating.

6. Method according to claim 5, wherein the plating liquid comprises an amount of fluorine containing particles, sufficient to obtain between 10 - 50 vol.-% of fluorine containing particles, relative to the total volume of the metallic film coating.

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7. Method according to any one of the preceding claims, wherein the plating comprises electroless plating.

8. Product with a wear resistant and smooth surface, provided by a metallic coating obtainable by a method according to any one of the preceding claims.

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9. Product, provided with a metallic coating, comprising particles, embedded in a metal matrix, the particles being distributed in a gradient throughout the thickness of the coating.

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10. Laundry iron, comprising a soleplate with a metallic coating, obtainable by a method according to any one of the preceding claims.

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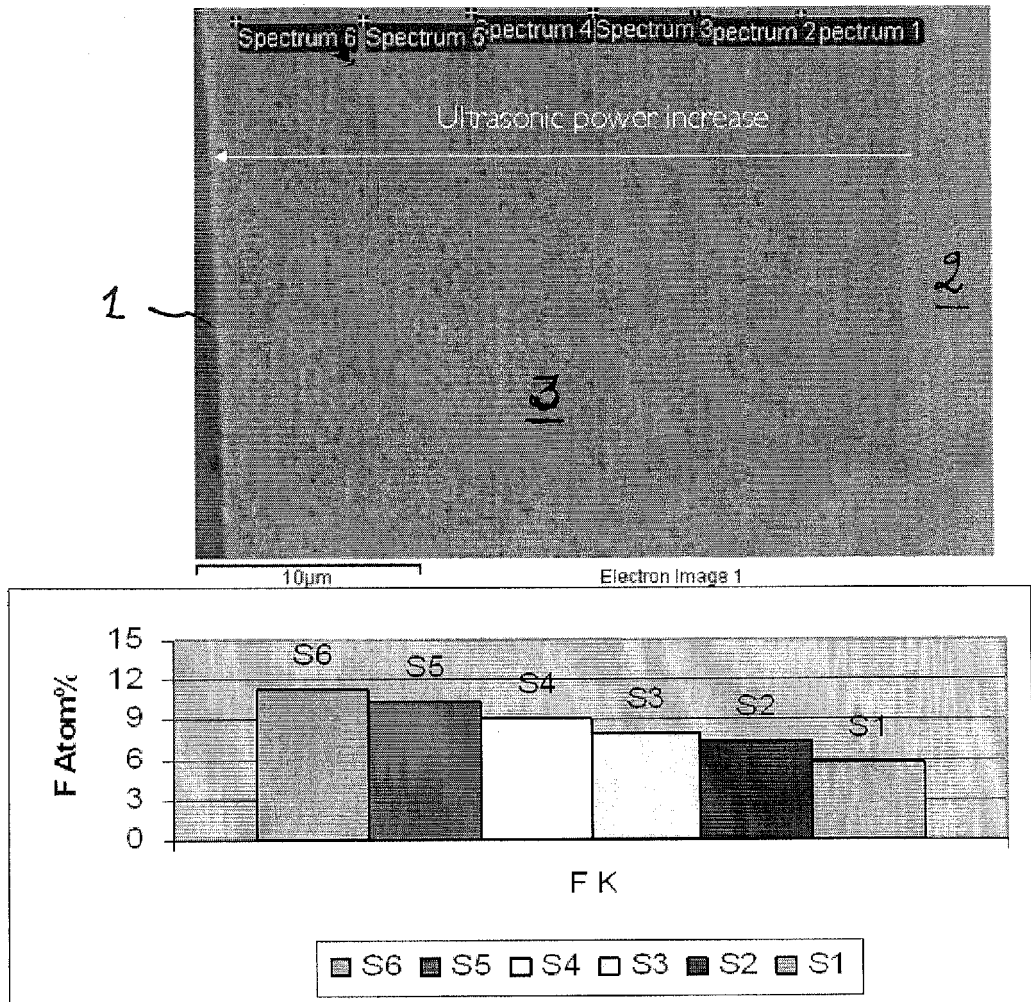


Fig. 1

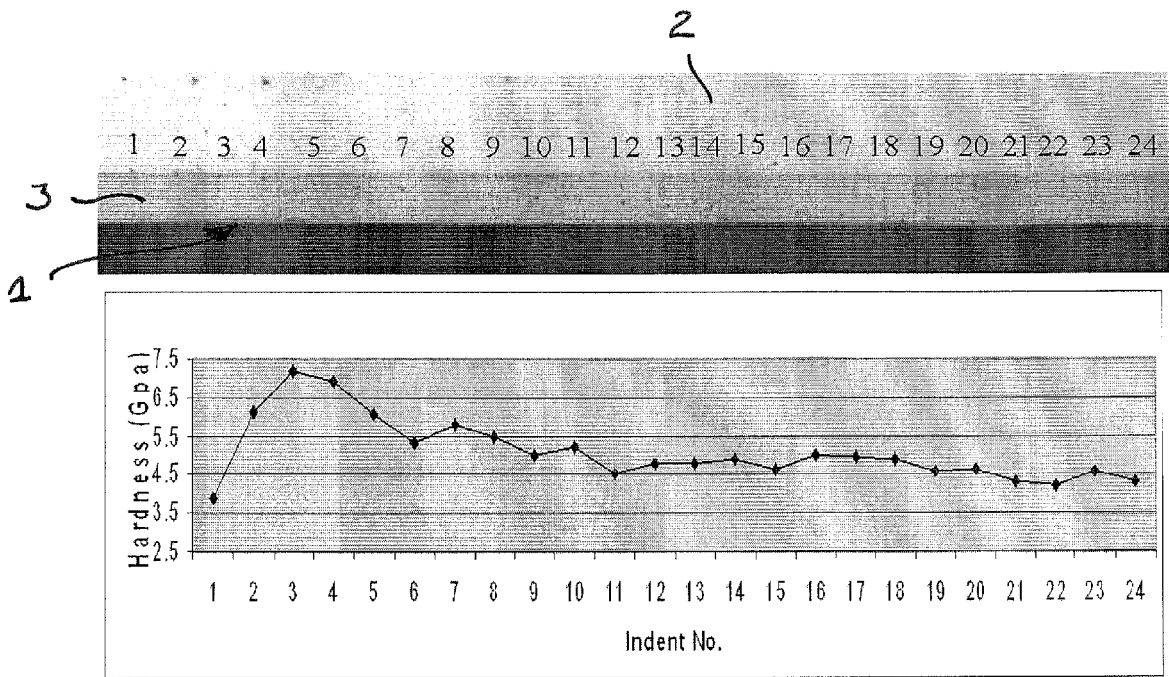


Fig. 2



EUROPEAN SEARCH REPORT

Application Number
EP 08 16 7819

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		9 April 2009	Le Hervet, Morgan
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

09-04-2009

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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