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

(11) EP 1 845 176 A1

(12) # EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
17.10.2007 Bulletin 2007/42

(21) Application number: **05793486.1**

(22) Date of filing: **17.10.2005**

(51) Int Cl.:
C25D 7/00 *(2006.01)* ***F02F 1/24*** *(2006.01)*
F02F 1/00 *(2006.01)* ***F01N 7/16*** *(2006.01)*
C25D 3/06 *(2006.01)* ***C25D 5/14*** *(2006.01)*
C25D 7/04 *(2006.01)*

(86) International application number:
PCT/JP2005/019037

(87) International publication number:
WO 2006/043507 (27.04.2006 Gazette 2006/17)

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

(30) Priority: **18.10.2004 JP 2004302479**

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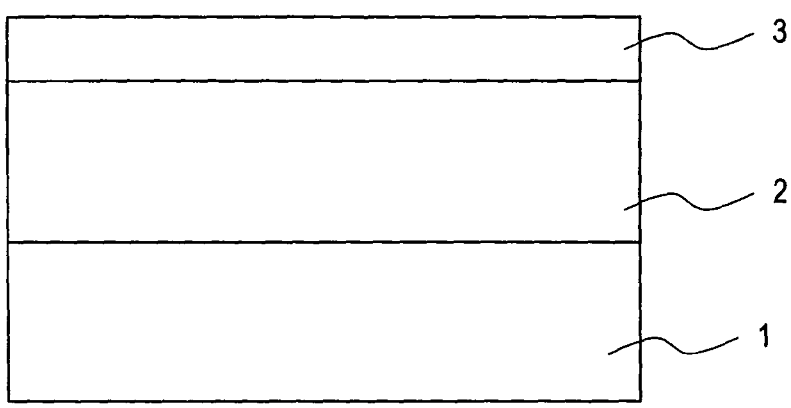
(54) **ENGINE PART**

(57) An engine part according to the present invention includes: a metal substrate; a chromium plating layer covering at least a portion of a surface of the metal substrate, the chromium plating layer being formed from a trivalent chromium plating solution. The chromium plating layer includes a boron content of no less than 0.05 mass% and no more than 0.3 mass%, and the chromium plating layer has a thickness or 0.7μm or less.

FIG. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to an engine part, and more particularly to an engine part which is subjected to a high temperature due to a high-temperature exhaust gas discharged from an engine.

BACKGROUND ART

[0002] In a vehicle such as a motorcycle or an all-terrain four-wheeled vehicle, not only the performance of the vehicle itself, but a good design is an important issue. FIG. 9 is a side view showing an example of a sports-type motorcycle. A motorcycle 200 shown in FIG. 9 includes a V-type engine 201 and an exhaust pipe 202 for guiding along exhaust gas. The V-type engine 201 includes cylinders 203, cylinder heads 204, and head covers 205. The aesthetically excellent V-type engine 201 is likely to be mounted to the motorcycle such that the engine is exposed on the outside, and is highly influential to the exterior appearance of the entire motorcycle.

[0003] Exhaust pipes extend from the two cylinders 203 of the V-type engine 201 and are united into the single exhaust pipe 202, which extends toward and above the rear wheel so as to allow exhaust gas to be discharged at the rear portion of the body. The exhaust pipe 202 must have a certain thickness for allowing the exhaust gas generated in the engine 201 to be efficiently discharged. Moreover, the portion constituting a muffler 202a has an increased diameter in order to accommodate the structure for muffling. For these reasons, the exhaust pipe accounts for a relatively large part of the exterior appearance of the entire motorcycle, and thus the shape and color of the exhaust pipe are highly influential to the entire motorcycle design.

[0004] In the present specification, engine components such as the cylinders 203, the cylinder heads 204, the head covers 205, and the exhaust pipe 202 for guiding the exhaust gas from the engine as well as a cover thereof, will be referred to as "engine parts". For the aforementioned reasons, the shape and color of engine parts are important factors in determining the entire motorcycle design.

[0005] Conventionally, those engine parts which show up on the exterior appearance are subjected to surface treatments such as plating to acquire a lustrous metallic color, thus to enhance the engine part design. Above all, decorative chromium plating has been widely used for engine parts because it is possible to give the plated material a characteristic, lustrous silver-gray color (see, for example, Patent Document 1).

[0006] Since decorative chromium plating provides an excellent metallic luster, and also excels in anticorrosiveness, it is also used in various fields other than engine parts. In order to obtain excellent exterior appearance and anticorrosiveness, it is unnecessary to form the decorative chromium plating so as to be thick. In fact, when formed thick, decorative chromium plating will result in a poor color tone and surface finish. Therefore, in general, decorative chromium plating is preferably used at a thickness in the range from 0.1 μm to 0.15 μm.

[0007] Note that, as plating using chromium, hard chromium plating (industrial chromium plating) is also widely used in industrial products. Since hard chromium plating has a low friction coefficient and an excellent abrasion resistance, it is used for sliding sections of various machine parts, for example. Since abrasion resistance is a requirement, hard chromium plating is usually formed to a thickness of several μm or more. Moreover, hard chromium plating does not have a decorativeness surface as does decorative chromium plating. Usually, decorative chromium plating has a surface roughness (Ra) of 1 μm or less (typically, 0.2 μm or less) after the plating, while hard chromium plating has a surface roughness of 1 μm or more.

[0008] Decorative chromium plating is usually formed by using a plating solution of chromate, including hexavalent chromium (Cr^{6+}). Hexavalent chromium is inexpensive, and a chromium plating layer formed from a plating solution containing hexavalent chromium (hereinafter referred to as a "hexavalent chromium plating solution") shows good contact with a base substrate, and has excellent anticorrosiveness and abrasion resistance. Furthermore, a chromium plating layer formed from a hexavalent chromium plating solution has a silver-gray color with a characteristically metallic luster. For these reasons, a hexavalent chromium plating solution is widely used for engine parts for motorcycles.

[0009] However, hexavalent chromium is known for its highly biotoxic nature. When performing plating with a hexavalent chromium plating solution, it has become a requirement that safety of the workers is ensured and that environmental pollution is prevented.

[0010] In order to solve such problems of hexavalent chromium, it is desired to use trivalent chromium (Cr^{3+}), which is less toxic than hexavalent chromium, to perform decorative chromium plating. Various plating solutions containing trivalent chromium have been proposed (Patent Documents 2 and 3).

Patent Document 1: Japanese Laid-Open Patent Publication No. 2003-41933

Patent Document 2: Japanese Laid-Open Patent Publication No. 52-065138

Patent Document 3: Japanese Laid-Open Patent Publication No. 52-092834

Patent Document 4: Japanese Laid-Open Patent Publication No. 9-95793

Patent Document 5: Japanese Laid-Open Patent Publication No. 9-228069

DISCLOSURE OF INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0011] From environmental and safety standpoints, it is preferable to use a plating solution containing trivalent chromium (hereinafter referred to as a "trivalent chromium plating solution"). However, a chromium plating layer which is formed by using a conventional trivalent chromium plating solution has a problem of being inferior to a plating layer which is formed from a hexavalent chromium plating solution, in terms of stability of growth of the chromium plating layer and the plating film-forming characteristics of the resultant chromium plating layer, e.g., anticorrosiveness and abrasion resistance.

[0012] Moreover, an engine part is heated to a high temperature due to heat generation associated with fuel combustion and a high-temperature exhaust gas. When a chromium plating layer is formed on an engine part by using a conventional trivalent chromium plating solution, there is a problem in that the chromium plating layer is likely to have cracks responsive to heating. If a crack occurs in a chromium plating layer, rust will occur from that portion, thus severely degrading the exterior appearance.

[0013] Therefore, trivalent chromium plating solutions of various compositions have been proposed since twenty or more years ago. However, trivalent chromium plating solutions have hardly been used for engine parts, in particular.

[0014] The present invention solves such conventional problems, and intends to provide an engine part having a chromium plating layer which is formed by using a trivalent chromium plating solution; which has as good film-forming characteristics as those of a plating layer that is formed from a hexavalent chromium plating solution; and which has excellent thermal resistance.

MEANS FOR SOLVING THE PROBLEMS

[0015] An engine part according to the present invention is an engine part comprising: a metal substrate; a chromium plating layer covering at least a portion of a surface of the metal substrate, the chromium plating layer being formed from a trivalent chromium plating solution, wherein, the chromium plating layer includes a boron content of no less than 0.05 mass% and no more than 0.3 mass%, and the chromium plating layer has a thickness or 0.7μm or less.

[0016] In a preferred embodiment, the boron content in the chromium plating layer is no less than 0.05 mass% and no more than 0.1 mass%.

[0017] In a preferred embodiment, the chromium plating layer includes an iron content of 2 mass% or less.

[0018] In a preferred embodiment, the chromium plating layer covers a region of the metal substrate surface that is heated to a temperature of 350˚C or more.

[0019] In a preferred embodiment, the engine part further comprises an underlying plating layer provided between the metal substrate surface and the chromium plating layer, wherein, the chromium plating layer has a thickness of no less than 0.2μm and no more than 0.7μm in the region that is heated to a temperature of 350˚C or more.

[0020] In a preferred embodiment, the underlying plating layer includes at least one of C and S.

[0021] In a preferred embodiment, the underlying plating layer further includes Ni.

[0022] In a preferred embodiment, the underlying plating layer is formed of a metal having a hardness lower than that of the Cr composing the chromium plating layer.

[0023] In a preferred embodiment, the underlying plating layer is formed from Ni plating.

[0024] In a preferred embodiment, the chromium plating layer has a color tone such that an L* value measured according to CIE (Commission Internationale de l'Eclairage) 1976 is in a range of no less than 68 and no more than 80.

[0025] In a preferred embodiment, the metal substrate is composed of a material containing Fe, A1, Zn, or Mg as a main component.

[0026] In a preferred embodiment, the metal substrate is a metal tube defining a passage through which an exhaust gas from an engine travels.

[0027] An engine according to the present invention comprises any of the aforementioned engine parts.

[0028] A transportation apparatus according to the present invention comprises any of the aforementioned engine parts or engine.

EFFECTS OF THE INVENTION

[0029] According to the present invention, a boron content in the chromium plating layer is adjusted to no less than 0.05 mass% and no more than 0.3 mass%, and the chromium plating layer has a thickness or 0.7μm or less. Therefore, by using a trivalent chromium plating solution, a chromium plating layer which has as good film-forming characteristics as those of a plating layer that is formed from a hexavalent chromium plating solution and which has good thermal resistance can be obtained. Thus, an engine part having good exterior appearance can be obtained by using a trivalent chromium plating solution.

[0030] Moreover, by prescribing a boron content in the chromium plating layer to be 0.1 mass% or less and an iron content to be 2 mass% or less, a silver-gray color tone similar to that of a chromium plating layer which is formed from a hexavalent chromium plating solution can be obtained. Furthermore, by prescribing the thickness of the chromium plating layer in a range of no less than 0.2μm and no more than 0.7μm, an engine part which is not likely to experience thermal discoloration can be obtained.

BRIEF DESCRIPTION OF DRAWINGS

[0031]

[FIG. 1] A diagram schematically showing the structure of an engine part according to the present invention.

[FIG. 2] (a) is a graph showing X-ray diffraction analysis results of a chromium plating layer formed by using trivalent chromium; and (b) is a graph showing X-ray diffraction analysis results of a chromium plating layer formed by using hexavalent chromium.

[FIG. 3] A diagram schematically showing the generation of a "C-S thickened layer" or a "C-S-Ni thickened layer", obtained by heating, near an interface between a chromium plating layer and an underlying plating layer.

[FIG. 4] (a) is a schematic diagram for explaining prevention of discoloration of a chromium plating layer by increasing the thickness of the chromium plating layer; and (b) is a diagram schematically showing a portion of a conventional chromium-nickel plating layer.

[FIG. 5] A side view showing a motorcycle in which an engine part according to the present invention is used.

[FIG. 6] (a) is a diagram schematically showing a portion of an exhaust pipe which is directly connected to an engine; (b) is a diagram schematically showing a cross section of a catalyst accommodating section of an exhaust pipe; and (c) is a diagram schematically showing a cross section of a manifold section.

[FIG. 7] A diagram showing an example of a chromium plating apparatus used in the present invention.

[FIG. 8] (a) is a diagram schematically showing an arrangement in which a minimum distance exists between a curved portion of a metal substrate and an electrode; and (b) is a diagram schematically showing an arrangement in which a long distance exists between a curved portion of a metal substrate and an electrode.

[FIG. 9] A side view showing the exterior appearance of a motorcycle.

DESCRIPTION OF THE REFERENCE NUMERALS

[0032]

30, 201	engine
4, 4a, 202	exhaust pipe
203	cylinder
204	cylinder head
205	head cover
1	metal substrate
2	underlying plating layer
3	chromium plating layer
5	metal tube

6	passage
7	silencer portion
8	catalyst
9	bent portion
9a	convex surface portion
9b	inner side face
10	plating layer
11	chromium plating trough
12	pump
13	percolator
14	adjustment valve
15	flowmeter
16	ion exchange apparatus
17	metal substrate
18	insoluble anode
19	DC power source
20	chromium plating apparatus
21	link section
22	catalyst accommodating section
23	another exhaust pipe
24	tube path
100, 200	motorcycle

BEST MODE FOR CARRYING OUT THE INVENTION

[0033] As a result of studying the composition of trivalent chromium plating solutions and the composition within resultant chromium plating layers, the inventor has found that the problem of cracks occurring in a chromium plating layer is related to the boron content within the chromium plating layer. The inventor has also found that the stability of growth of a chromium plating layer and the anticorrosiveness and abrasion resistance of the resultant chromium plating layer are also related to the boron content within the chromium plating layer and the boron concentration within the trivalent chromium plating solution.

[0034] Moreover, a chromium plating layer which is formed from a conventional trivalent chromium plating solution has a blackish color tone as compared to a chromium plating layer which is formed from a hexavalent chromium plating solution. This has been found to be related to the iron content in the resultant chromium plating layer.

[0035] Furthermore, when providing on an engine part a chromium plating layer which is formed from a trivalent chromium plating solution, the surface color tone may change due to heating, so that the chromium plating layer may appear blue-violet. Such discoloration will degrade the exterior appearance of a motorcycle or the like in which the engine part is mounted. The inventor has found that the discoloration of a chromium plating layer due to heating depends on the thickness of the chromium plating layer.

1. Structure of the engine part

(1) Basic structure

[0036] Hereinafter, with reference to FIG. 1, the structure of an engine part according to the present invention will be described. As shown in FIG. 1, the engine part according to the present invention includes a metal substrate 1, a chromium plating layer 3 covering at least a portion of the surface of the metal substrate 1, and an underlying plating layer 2 provided between the metal substrate 1 and the chromium plating layer 3. Hereinafter, these constituent elements will be specifically described.

(i) Metal substrate

[0037] The metal substrate 1, which has a mechanical strength suitable to its purpose and a necessary level of anticorrosiveness and the like, can be formed from a material which is usually used for an engine part. A typical example would be an Fe-type material. Otherwise, the metal substrate 1 may be formed from any non-Fe material, such as an Al-type material, a Zn-type material, an Mg-type material, or a Ti-type material.

[0038] Examples of Fe-type materials include Fe or steels whose main component is Fe, such as: steel tubes for machine structural purposes (e.g., carbon steel tubes for machine structural purposes (STKM) or alloy steels for machine structural purposes); stainless steel (e.g., ferrite-type stainless steel, austenite-type stainless steel, or austenite/ferrite-type stainless steel); and mild steel (e.g., SPCC or SPHC). Examples of Al-type materials include: Al; and Al alloys such as Al-Si alloys or Al-Si-Mg-type alloys.

Examples of Zn-type materials include: Zn; Zn-plated steel plates, on which Zn plating is provided; and Zn alloy-plated steel plates, on which Zn alloy plating whose main component is Zn and which includes alloying elements such as Ni, Co, Cr, or Al is provided. Examples of Mg-type materials include Mg-Al type alloys and Mg-Zn type alloys. Examples of Ti-type materials include: Ti; and Ti alloys whose main component is Ti and which includes elements such as Al, V, or Si.

[0039] These materials have different characteristics depending on their types. For example, Al is light-weight and shiny, whereas Ti is light-weight and has excellent mechanical strength. Therefore, any appropriate material may be selected depending on the purpose, required characteristics, and the like.

(ii) Underlying plating layer

[0040] The underlying plating layer 2 formed on the metal substrate 1 defines an underlying plating for the chromium plating layer 3. From the standpoint of preventing cracks from occurring in the chromium plating layer and allowing a chromium plating layer having good anticorrosiveness and abrasion resistance to stably grow, the underlying plating layer 2 does not need to be provided. In the case of chromium plating, an underlying plating layer is usually formed under the chromium plating layer with the purpose of providing enhanced contact with the base substrate, for example. Therefore, it is preferable that the underlying plating layer 2 exhibits good contact with various metal substrates, as well as good contact with the chromium plating layer. There might be other preferable characteristics, e.g., anticorrosiveness.

[0041] The metal composing the underlying plating layer 2 used for the present invention can be defined in terms of a relationship with the hardness (Vickers hardness) of chromium, which is used for forming the chromium plating layer. Specifically, it is preferable that the metal composing the underlying plating layer 2 is formed of a metal having a hardness lower than the hardness of chromium (about 350 to 1200 Hv). The presence of a layer composed of a low-hardness metal interposed between the chromium plating layer and the metal substrate reduces the stress applied to the chromium plating layer due to heat cycles. As a result, the generation of cracks and the like is prevented, and a chromium plating layer having good surface characteristics can be obtained. Examples of metals having a lower hardness than that of chromium include nickel (Ni) (hardness: about 150 to 350 Hv), Copper (Cu) (hardness: about 40 to 250 Hv), Tin (Sn) (hardness: about 20 to 200 Hv), and lead (Pb) (whose hardness is immeasurable).

[0042] As an underlying plating layer including such metals, for example, a layer composed of nickel plating, copper plating, tin plating, lead plating, zinc-nickel plating, or the like is used. A single such plating layer may be formed, or two or more kinds may be combined to result in there being a plurality of underlying plating layers. Alternatively, a plurality of underlying plating layers of the same kind but containing different types of additives, etc., may be formed. A typical underlying plating layer to be used as the underlying treatment for a chromium plating layer is nickel plating, which further enhances anticorrosiveness, luster, and the like.

[0043] The underlying plating layer 2 includes elements which compose various additives. With the purpose of enhancing the luster of the chromium plating layer, such additives are added in a plating solution for forming the underlying plating layer 2. Specifically, a primary brightener (a non-butyne-type brightener, e.g., saccharin sodium, naphthalene-1,3,6-trisodium trisulfonate, or benzene sulfonic acid), a secondary brightener (e.g., 2-butyl-1,4-diol, sodium allylsulfonate), and the like are used. Any such additive includes C and/or S as its component elements. Although depending on the type of underlying plating layer and the type of additive, a total of about 0.001 to 1.0 mass% of C and/or S is included in the underlying plating layer. As will be specifically described later, these elements will thicken to about 0.1 to 10 mass% responsive to heating, thus causing surface discoloration of the chromium plating layer. Furthermore, in the case where the underlying plating layer 2 is a nickel plating layer, the Ni contained in the nickel plating layer also substantially affects surface discoloration.

[0044] Hereinafter, nickel plating will be specifically described as a typical example of an underlying plating layer. Nickel plating is generally classified into lusterless nickel plating, semigloss nickel plating, and gloss nickel plating, mainly depending on the type of brightener added in the plating solution, whether such an addition is made or not, etc. These types of plating can be appropriately combined in accordance with the required characteristics, purpose, and the like, whereby the desired exterior appearance can be obtained.

[0045] Among others, gloss nickel plating is obtained by adding a brightener such as saccharin or benzene sulfonic acid to the plating solution. Gloss nickel plating provides an excellent surface leveling (planarize) action and exhibits good contact with the chromium plating layer, and therefore is widely used as an underlying layer to be formed directly under a chromium plating layer. A brightener for gloss nickel plating is usually used in an amount such that a total of about 0.001 to 1.0 mass% of at least one of C and S is included in the plating layer. Anticorrosiveness tends to decrease as the S content increases.

[0046] Lusterless nickel plating differs from gloss nickel plating in that no brightener is contained in the plating solution. Although providing less luster than gloss nickel plating, lusterless nickel plating is excellent in terms of throwing power (adhesion), anticorrosiveness, discoloration prevention, etc., of the plating layer.

[0047] Semigloss nickel plating is obtained by adding a non-coumarin-type semi-brightener to the plating solution. Unlike the aforementioned brighteners, semi-brighteners have little C and/or S content. Therefore, it provides better anticorrosiveness but poorer luster than those provided by gloss nickel plating.

[0048] In general, when a number of nickel plating layers containing different amounts of S are formed on top of one another, potential differences will emerge between the plating layers, so that coatings having greater S contents are corroded first. By utilizing this property, it is common to use two or more layers of nickel plating to provide improved anticorrosiveness. For example, in the case of a two-layer plating obtained by sequentially forming a semigloss nickel plating layer and a gloss nickel plating layer upon a base metal, the gloss plating layer is corroded first because of having a lower potential than that of the semigloss plating layer. As a result, the base metal under the semigloss plating layer is protected without being corroded. In order to further enhance anticorrosiveness in the aforementioned two-layer plating structure, a tri-nickel plating layer (which is a type of gloss nickel plating layer) having a large S content may be formed between the semigloss nickel plating layer and the gloss nickel plating layer, thus obtaining a three-layer plating structure. The S contained in the tri-nickel plating layer is most often supplied from an additive other than a brightener. In this case, the uppermost gloss nickel plating layer is corroded first, and then the intermediate tri-nickel plating layer is corroded, whereby both the semigloss nickel plating layer and the base metal are protected.

[0049] In order to effectively utilize such actions of nickel plating, the nickel plating layer(s) preferably has a total thickness of about 10 to 30 μm, and more preferably about no less than 15 μm and no more than 25 μm.

[0050] In the case where an underlying plating layer other than a nickel plating layer is to be formed, the underlying plating layer is preferably controlled to a thickness of about 10 to 30 μm.

(iii) Chromium plating layer

[0051] On the underlying plating layer 2, the chromium plating layer 3 is formed. As will be specifically described later, the chromium plating layer 3 is a decorative chromium plating layer which is formed by electroplating using a trivalent chromium plating solution.

[0052] Whether a chromium plating layer has been formed by using a trivalent chromium plating solution or by using a hexavalent chromium plating solution can be determined by measuring the crystal state of the chromium plating layer. Specifically, the determination can be easily made by subjecting the chromium plating layer to an X-ray diffraction analysis. FIGS. 2(a) and (b) each show X-ray diffraction analysis results of a chromium plating layer. The detailed measurement method was as follows.

[0053] Analysis equipment: X-ray diffraction apparatus RAD-3C type (Rigaku Corporation)
Measurement conditions: A Cu anticathode was used, and power was supplied at 40kV/40mA.
X-ray diffraction results of a chromium plating layer which has been formed by using a hexavalent chromium plating solution are shown in FIG. 2(b). Near diffraction angles of about 40θ to 50θ, a very large diffraction peak of about 1200 cps is observed, and large diffraction peaks of about 200cps are observed near diffraction angles of about 65 θ and about 83 θ . In the ascending order of diffraction angles, these peaks correspond to (111) orientation crystal, (200) orientation crystal, and (211) orientation crystal, respectively.

[0054] On the other hand, X-ray diffraction results of a chromium plating layer which has been formed by using a trivalent chromium plating solution are shown in FIG. 2(a). Only a small diffraction peak of about 100 cps is observed near diffraction angles of about 40 to 50 θ, this corresponding to (111) orientation crystal. A value obtained by dividing the half-width of the peak corresponding to (111) orientation crystal by the peak intensity (half-width/peak height) is about 0.6rad/cps, which is much broader than the value of (111) orientation crystal (about 7.9×10^{-4}rad/cps) which is observed when using hexavalent chromium.

[0055] From these figures, it can be seen that the chromium plating layer obtained by using hexavalent chromium has a crystal structure composed of polycrystals, whereas the chromium plating layer obtained by using trivalent chromium plating solution has a substantially amorphous structure. The determination as to whether a plating layer has a crystalline structure or an amorphous structure can be made based on, for example, whether a diffraction peak associated with a (half-width/peak height) value of about 0.001 rad/cps or less is observed or not near diffraction angles of about 40 to 50 θ.

[0056] The amount of boron contained in the chromium plating layer 3 is no less than 0.05 mass% and no more than 0.3 mass%. If the boron content is more than 0.3 mass%, cracks may occur in the chromium plating layer 3 responsive to heating to 400 ˚C or above. On the other hand, if the boron content is less than 0.05%, the anticorrosiveness and abrasion resistance of the chromium plating layer 3 become lowered. Moreover, stability of plating growth when forming the chromium plating layer 3 becomes lower. The boron content is preferably no less than 0.05 mass% and no more than 0.2 mass%, and more preferably no less than 0.05 mass% and no more than 0.1 mass%. Crack generation can be prevented with more certainty and better anticorrosiveness and abrasion resistance can be obtained as there is less boron content.

[0057] Herein, "stability of plating growth" means that the throwing power (adhesion) of a chromium plating layer in a plating process is constant over time. Specifically, it means that, when a Hull cell test is conducted, poor exterior appearance, e.g., inadequate plating thickness, scorching, or streaks, is prevented over a large area of current density, or that a plating layer with a predetermined thickness is formed also on portions of the material to be plated that are difficult to be plated (e.g., a surface to be plated that is located opposite from an electrode).

[0058] Moreover, "plating anticorrosiveness" means an anticorrosiveness that is imparted through a plating process. Specifically, if a resting number of 7.0 or more is satisfied when performing a CASS test (which is a plating anticorrosiveness test method defined in JIS H8502) by using a sample that has experienced a plating process, it is said that "there is good plating anticorrosiveness".

[0059] "Plating abrasion resistance" means an abrasion resistance (hardness) that is imparted through a plating process. Specifically, if the Vickers hardness is in the range of 350Hv0.1 (test power: 0.9807N) or more when a Vickers hardness as defined in JIS Z 2244 is measured by using a sample that has experienced a plating process, it is said that "there is good plating abrasion resistance".

[0060] Thus, since the chromium plating layer 3 contains boron, a chromium plating layer having good anticorrosiveness and abrasion resistance can be obtained. Moreover, the chromium plating layer can be allowed to stably grow. However, boron acts to harden the plating layer, and, if its content exceeds the aforementioned range, the hardness of the chromium plating layer will increase especially when heated to a high temperature (esp., 400˚C or more), so that the stress on the chromium plating layer due to heat cycles will be increased. As a result, cracks and the like are likely to occur on the surface. If cracks occur, rust is likely to occur from the cracks. If a large number of cracks occur, coating may peel, etc., thus degrading the exterior appearance. Moreover, the color tone will be degraded when the content exceeds the aforementioned range.

[0061] As described above, since boron causes the chromium plating layer to be hardened, cracks become likely to occur when a thick chromium plating layer containing boron is formed. Therefore, the thickness of the chromium plating layer 3 is preferably 0.7μm or less. If the chromium plating layer 3 is thicker than 0.7μm, it becomes difficult to form a chromium plating layer without cracks even if the boron content is within the aforementioned range. In order to more certainly prevent crack generation, it is preferable that the thickness of the chromium plating layer 3 is 0.5 μm or less.

[0062] From the standpoint of preventing crack generation due to heating, it will suffice that the boron content in the chromium plating layer is kept at 0.3 mass% or less only in regions of the engine part that will rise to a high temperature. However, in any chromium plating layer which is to continuously cover the surface of an engine part through plating, it is difficult to vary the boron content in a portion thereof. Therefore, it is preferable that the boron content in the chromium plating layer remains within the aforementioned range in any region of the chromium plating layer.

[0063] However, just because the boron content remains within the aforementioned range in any region of the chromium plating layer, it is not necessary for the engine part according to the present invention to be used in an environment where its entirety is heated to a high temperature. The present invention is suitably used for an engine part at least a portion of which is exposed to a high temperature.

[0064] So long as the chromium plating layer 3 has a boron content as described above, it is possible, by using a trivalent chromium plating solution, to form a chromium plating layer which has as good film-forming characteristics as those of a plating layer formed from a hexavalent chromium plating solution and which has good thermal resistance. However, a chromium plating layer which is formed from a trivalent chromium plating solution has a blackish color tone as compared to a chromium plating layer which is formed from a hexavalent chromium plating solution. The causes for the blackish color tone are related to the concentrations of iron and boron that are contained in the chromium plating layer. The color tone becomes blackish particularly when the iron content increases. Although not clearly known, it is believed that, when growing a chromium plating layer from a trivalent chromium plating solution, the iron within a chromium plating layer binds with various elements within the plating solution, thus generating a deposit containing black iron.

[0065] Therefore, in order to a silver-gray color tone similar to a chromium plating layer which is formed from a hexavalent chromium plating solution, the boron content is preferably 0.1 mass% or less and the iron content is 2 mass% or less in the chromium plating layer 3. The iron content should be as little as possible, and is more preferably 1 mass% or less, and further more preferably 0.5 mass% or less.

[0066] However, in the case where the engine part according to the present invention is not to be used in a manner of being compared against a chromium plating layer which is formed from a hexavalent chromium plating solution, the boron content may be prescribed to be 0.3 mass% or less and the iron content to be 7 mass% or less, whereby a chromium plating layer with a color tone that qualifies for chromium plating can be obtained, although its color tone may be somewhat muddier.

[0067] The boron and iron contents in the chromium plating layer are to be each expressed as a maximum value when the content of each element, contained along the depth direction of the chromium plating layer, is analyzed through GDS analysis.

[0068] In the case where the boron content is 0.1 mass% or less and the iron content is 2 mass% or less in the chromium plating layer 3, the chromium plating layer has a color tone such that an L* value measured according to CIE (Commission Internationale de l'Eclairage) 1976 is in a range from 68 to 80. The L value is to be measured by using a spectrometric color difference meter (e.g., color analyzer TC-1800MK-II (Tokyo Denshoku)). This value is similar to that of a chromium plating layer which is formed from a hexavalent chromium plating solution. Therefore, even in a side-by-side comparison between the chromium plating layer 3 whose iron content is confined within the aforementioned range and a chromium plating layer which is formed from a hexavalent chromium plating solution, hardly any difference in color tone will be noticed.

[0069] Since the engine part has such a structure, it is possible, by using a trivalent chromium plating solution, to obtain a chromium plating layer which has as good film-forming characteristics as those of a plating layer which is formed from a hexavalent chromium plating solution and which has good thermal resistance. Moreover, by prescribing the boron content to be 0.1 mass% or less and the iron content to be 2 mass% or less in the chromium plating layer, a silver-gray color tone similar to that of a chromium plating layer which is formed from a hexavalent chromium plating solution can be obtained.

[0070] (iv) Mechanism of discoloration prevention

The engine part according to the present invention can be suitably used in parts of an engine; e.g., a cylinder, a cylinder head, and a head cover; an exhaust pipe for guiding along exhaust gas from the engine; and the like. However, in the case where the engine part according to the present invention is used in a place which is exposed to a heat of 350˚C or above, the color tone of the surface may change due to heating, so that the chromium plating layer may appear blue-violet. In the case where the engine part according to the present invention is used in such a place, it is preferable that the chromium plating layer has a thickness of 0.2 μm or more. Hereinafter, the reason why discoloration of the chromium plating layer due to heating can be prevented by controlling the thickness of the chromium plating layer will be described with reference to FIG. 3 and FIG. 4.

[0071] FIG. 3 is a diagram schematically showing a manner in which C and/or S gather near the interface between the chromium plating layer and the underlying plating layer responsive to heating, thus showing a generation mechanism of a "C-S thickened layer" or a "C-S-Ni thickened layer" (hereinafter may simply be referred to as a "thickened layer"), which is considered as responsible for the surface discoloration of the chromium plating layer. FIG. 3 illustrates a typical structure according to the present invention, in which a nickel plating layer is formed between an Fe substrate and a chromium plating layer. The nickel plating layer is composed of the following three layers, respectively from the Fe substrate side: a semigloss nickel plating layer, a tri-nickel plating layer, and a gloss nickel plating layer.

[0072] Note that, responsive to heating, various elements which compose the additives contained in the chromium plating layer and/or the nickel plating layer will gather near the interface between the chromium plating layer and the nickel plating layer. FIG. 3 only shows those elements which are considered as contributive to the discoloration of the chromium plating layer, i.e., the elements (at least one of C, S, and Ni) composing the aforementioned thickened layer and elements (e.g., Fe or Cr) which are likely to bind to these elements, while omitting any other elements (e.g., O which gathers near the aforementioned interface responsive to heating).

[0073] As shown in FIG. 3, mainly C or S moves from the nickel plating layer side to the chromium plating layer side, thus gathering at the aforementioned interface. As described earlier, C or S is mainly the element which composes a non-butyne-type brightener (e.g., benzene sulfonic acid) which is added to the nickel plating solution. In particular, a large amount of S is contained in the gloss nickel plating layer and the tri-nickel plating layer. Therefore, near the aforementioned interface, a "C-S thickened layer" in which a large amount of C or S has gathered is formed. As used herein, a "C-S thickened layer" means a layer in which at least one of C and S has gathered. Note that, although C or S may also diffuse over from the chromium plating layer side, such diffusion will account for a very small proportion as compared to the diffusion from the nickel plating layer side, and therefore is omitted from illustration.

[0074] In the case where the underlying plating layer is a nickel plating layer, a "C-S-Ni thickened layer" containing Ni will be formed. Similarly to C or S, Ni is also considered as contributive to discoloration. As used herein, a "C-S-Ni thickened layer" means a layer in which at least one of C or S and Ni has gathered.

[0075] Although not clearly known, the reason why formation of such a thickened layer causes surface discoloration of the chromium plating layer may be that the Cr composing the chromium plating layer may bind to the element (C or S, or Ni) composing the thickened layer and change the refractive index of the chromium plating layer, thus causing discoloration, for example. Iron is also considered as a substance that contributes to discoloration. In the case where the metal substrate is composed of an Fe-type material, responsive to heating, Fe may diffuse from the Fe-type material and become thickened in the area of the aforementioned interface (not shown).

[0076] Surface discoloration of the chromium plating layer associated with such a thickened layer can be prevented by forming the thickness of the chromium plating layer to be 0.2 μm or more. Hereinafter, the reason thereof will be described with reference to FIGS. 4(a) and (b).

[0077] FIG. 4(b) is a diagram schematically showing a portion of a conventional Cr-nickel plating layer. As shown in FIG. 4(b), the thickness of the conventional chromium plating layer is as small as about 0.1 μm or less. Therefore, incident light will be transmitted to the vicinity of the interface between the chromium plating layer and the nickel plating layer. Consequently, a portion of the incident light will be absorbed by the thickened layer which is generated near the interface, thus making the discoloration due to heating more conspicuous.

[0078] On the other hand, by prescribing the thickness of the chromium plating layer to be 0.2 μm or more, as shown in FIG. 4(a), the incident light will for the most part be reflected near the surface of the chromium plating layer, instead of being transmitted over to the vicinity of the interface between the chromium plating layer and the nickel plating layer. Therefore, only the interference colors caused by the usually-occurring oxide coating on the outermost surface of a chromium plating layer are observed, and the influence due to the thickened layer can be minimized.

[0079] In order to allow such action to be effectively exhibited, the thickness of the chromium plating layer is set to be 0.2 μm or more. From the perspective of prevention of thermal discoloration due to heating, the chromium plating layer should be as thick as possible. Preferably, the thickness of the chromium plating layer is 0.3 μm or more, and more preferably 0.4 μm or more.

[0080] Thus, in order to prevent crack generation and discoloration due to heating, the thickness of the chromium plating layer is preferably no less than 0.2μm and no more than 0.7μm, and more preferably no less than 0.3μm and no more than 0.5μm. When the thickness of the chromium plating layer is no less than 0.4μm and no more than 0.5μm, crack generation can be almost surely prevented, and discoloration due to heating can be surely prevented.

[0081] The thickness of the chromium plating layer 3 may be measured through observation with an optical microscope (magnification: × 400). Specifically, a cross section along the thickness direction of the plating layer is mirror-polished and etched. As a result, the chromium plating layer becomes clearly distinguishable from the underlying plating layer. Note that the chromium plating layer will have a surface roughness Ra of not more than about 0.01 μm, and therefore the influence of the surface roughness Ra on the thickness of the chromium plating layer is virtually negligible. Since the thickness of the chromium plating layer will slightly vary depending on the measurement site, a total of three measurements are to be taken in different measurement sites within a given a field of observation, and an average value thereof is to be defined as the "thickness of the chromium plating layer".

[0082] Another means for preventing discoloration due to the formation of a thickened layer might be to reduce the C or S content, although this method would not be practical. For example, in order to reduce the C or S content, the amount of brightener to be contained in the underlying plating layer would mainly have to be reduced. However, this would result in a reduced luster, and thus considerably impair the design of the engine part. When good design is considered as an important factor as in the case of the present invention, any deterioration in design because of not using the brightener must definitely be avoided.

[0083] In order to prevent discoloration due to heating, it will suffice if a portion of the chromium plating layer 3 which is to be heated to a temperature of 350˚C or above satisfies the aforementioned range of thickness. It is not necessary that the entire area of the chromium plating layer 3 formed on the metal substrate 1 satisfy the aforementioned range of thickness. In regions which will only rise to a temperature of 350 ˚C or less, the thickness of the chromium plating layer 3 may be 0.2 μm or less. In general, a chromium plating layer is tinted from silver-gray to yellow to gold responsive to heating, and at a high temperature of about 350 to 500˚C, becomes discolored from gold to violet. Such changes in color tone will not be uniformly observed over the entire area in which the chromium plating layer is formed, but will be most noticeable in portions which are likely to be exposed to a high-temperature exhaust gas. Therefore, in order to prevent discoloration from gold to violet, it will be sufficient to control the thickness of the portion at which discoloration due to heating is most likely to occur, i.e., the region of the chromium plating layer that is exposed to a temperature of 350 ˚C or above, to be in the aforementioned range.

[0084] Examples of the "region which is to be heated to a temperature of 350˚C or above" may include a portion of an engine part composing an engine, e.g., a cylinder, a cylinder head, a head cover, as well as a portion of an exhaust pipe defining a channel for guiding the exhaust gas discharged from the engine, or a cover of the exhaust pipe. As used herein, the exhaust pipe may be an exhaust pipe which directly guides exhaust gas, or an exhaust pipe (a double tube) which is indirectly heated by exhaust gas. An exhaust pipe includes a manifold section for guiding along the exhaust gas from each cylinder, a catalytic apparatus accommodating section covering a catalytic apparatus, a muffler, and the like.

(2) Specific structure and application to motorcycle

[0085] With reference to FIG. 5, a specific structure of the engine part according to the present invention will be described. FIG. 5 shows a motorcycle 100 incorporating an exhaust pipe which is an engine part according to the present invention. As shown in FIG. 5, the motorcycle 100 includes an engine 30 which is composed of a 4-cycle internal combustion engine, and an exhaust pipe 4 for guiding the exhaust gas generated in the engine 30 so as to be discharged at the rear portion of the body. The exhaust pipe 4 includes an exhaust pipe congregation section 4a, which is connected to the engine 30 and constitutes a substantially bent exhaust path for allowing the exhaust gas having been discharged at the front of the engine 30 to be guided toward the rear, and a muffler 4b. The exhaust pipe congregation section 4a may be integrally formed of a single part, or composed of a plurality of parts which are connected with one another. In the present embodiment, the exhaust pipe 4 is entirely exposed so as to appear on the exterior of the motorcycle 100, thus constituting a part of the design of the motorcycle 100 as a whole. As will be specifically described below, the effect of the present invention, i.e., cracks or rust does not occur in the chrome plating layer of the exhaust pipe 4, discoloration is prevented, and the fresh exterior appearance of a brand-new motorcycle is retained for long periods of time, is more clearly enhanced in the exterior appearance in the case where the entire exhaust pipe 4 is exposed. However, as long as the exhaust pipe 4 at least partially appears on the exterior, a part of the exhaust pipe 4 may be covered by a cowl or a protector, depending on the design of the motorcycle. Moreover, the shape of the motorcycle for which the exhaust pipe is used is not limited to that shown in FIG. 5. For example, the exhaust pipe according to the present invention may be adopted in a motorcycle having a structure as shown in FIG. 9.

[0086] Next, with reference to FIGS. 6(a), (b), and (c), the "region of the metal substrate surface that is to be heated to a temperature of 350˚C or above", on which the chromium plating layer preferably has a thickness of 0.2 μm or more, will be described. Each of these figures is a cross-sectional view showing a part of the exhaust pipe 4.

[0087] FIG. 6(a) shows an exhaust pipe congregation section 4a of the exhaust pipe 4, which is directly connected to an engine. As shown in FIG. 6(a), the exhaust pipe congregation section 4a, which is connected to an engine (not shown), includes a metal tube 5 defining a passage 6 in which exhaust gas travels through, and a plating layer 10 covering the outer side surface of the metal tube 5. The metal tube 5 includes a bent portion 9. The bent portion 9 is a portion at which the passage 6 is bent, or a portion at which the longitudinal direction of the passage 6 changes.

[0088] As described above, the plating layer 10 includes an underlying plating layer and a chromium plating layer. The metal tube 5 simply needs to define the passage 6, and may have a double-tube structure composed of an inner tube defining the passage 6 and an outer tube covering the inner tube from the outside.

[0089] The exhaust gas that comes through the exhaust pipe congregation section 4a, which is directly connected to the engine (not shown), rapidly travels through the passage 6, and therefore collides against the metal tube 5 at the bent portion 9. The exhaust gas collides especially intensely against an inner side surface 9b of the metal tube 5 that is located at the convex surface portion 9a, which in itself is formed as a result of the bending. Therefore, the outer convex surface portion 9a is heated by the high-temperature exhaust gas to a temperature of about 350 ˚C or more (e.g., about 400 to 500˚C).

[0090] In the case where the metal tube 5 has a double-tube structure, a single-tube structure is often adopted for a link section 21 at which another exhaust pipe member 23 is to be connected. The reason is that, if a double-tube structure were adopted at the link section 21, the metal tube 5 might deform or be destroyed due to a difference in thermal expansion between the outer tube and the inner tube during the welding to the other exhaust pipe member 23. If the metal tube 5 is of such a structure, the link section 21 will be heated to a temperature of about 350˚C or more (e.g., about 400 to 500˚C) as the high-temperature exhaust gas comes in direct contact with the inner side surface of the link section 21.

[0091] FIG. 6(b) schematically shows a cross section of a catalyst accommodating section 22 of the exhaust pipe 4, in which a catalytic apparatus 8 is accommodated. The catalytic apparatus 8 which is provided within the catalyst accommodating section 22, decomposes at least one component contained in the exhaust gas when the exhaust gas travel therethrough. Since the catalytic apparatus 8 is heated responsive to the aforementioned decomposition, the catalyst accommodating section 22 is heated to a temperature of about 350˚C or more (e.g., about 400 to 500˚C).

[0092] In the case where the engine 30 (FIG. 5) has a plurality of cylinders, the exhaust pipe 4 may include a manifold section for combining the exhaust gas generated in the respective cylinders so as to allow such exhaust gas to be guided to the rear portion of the motorcycle 100. FIG. 6(c) shows an exhaust pipe 4 having a manifold section 15 at which branch pipes 4d and 4e (each of which is connected to a cylinder) come together, such that discharge takes place through a unified exhaust pipe member 4f. At such a manifold section 15 of the exhaust pipe congregation section 4a, exhaust gas comes together through the plurality of branch pipes 4d and 4e, whereby the flow rate of the exhaust gas is increased, and the flow paths are deflected. As a result, the exhaust gas collides against the inner side surface of the manifold section 15. Therefore, the manifold section 15 is heated by the exhaust gas to a temperature of about 350˚C or more (e.g., about 400 to 500˚C).

[0093] In the motorcycle of the present embodiment, those portions of the exhaust pipe which are exemplified as being heated to a high temperature in FIGS. 6(a), (b), and (c) are covered from the outside by a chromium plating layer of 0.2 μm or more. As a result, even when exposed to a high-temperature exhaust gas, discoloration of the chromium plating layer due to the heating can be prevented.

[0094] In the case of using a chromium plating layer which is formed by using trivalent chromium, the Fe content in the chromium plating layer is reduced. As a result, an excellent color tone similar to that which is obtained by using hexavalent chromium can be expressed.

[0095] The present invention also encompasses a transportation apparatus incorporating the above-described engine part(s). Examples of transportation apparatus include a vehicle having an engine (e.g., a motorcycle or an all-climate four-wheeled vehicle) and a transportation apparatus having an engine (e.g., a marine vessel or an airplane).

2. Method of producing the engine part

[0096] Next, a method for producing an engine part according to the present invention will be described. The engine part according to the present invention is produced by sequentially forming an underlying plating layer and a chromium plating layer on a metal substrate having a predetermined shape. Hereinafter, the production method will be specifically described.

[0097] First, in order to degrease and clean the surface of a metal substrate, a metal substrate is immersed in a bath such as a water rinse bath, ultrasonic wave alkaline degreasing bath, electrolytic degreasing bath, or acid treatment activation bath for a predetermined period of time. As a result of this, the surface of the metal substrate is sufficiently degreased, thus making it easy to form an underlying plating layer and a chromium plating layer on the metal surface.

[0098] Next, by using the metal substrate thus washed, an electroplating is conducted to sequentially form an underlying plating layer and a chromium plating layer at least on the outer surface of the metal substrate. Both the underlying plating layer and the chromium plating layer are to be formed through electroplating, based on the same principle. Therefore, in the following description, only the step of forming the chromium plating layer will be specifically described by using the plating apparatus shown in FIG. 7, whereas the step of forming the underlying plating layer will be described without referring to any figures.

[0099] The underlying plating layer is formed by immersing the aforementioned metal substrate in a plating trough containing a solution of a metal from which a plating layer is to be formed, and applying power until reaching a desired thickness. For example, in the case where three nickel plating layers, namely a semigloss nickel plating layer, a tri-nickel plating layer, and a gloss nickel plating layer, are to be formed as the underlying plating layer, the metal substrate which has been washed in the aforementioned manner is immersed in a semigloss nickel plating solution, a tri-nickel plating solution, and a gloss nickel plating solution, and power is applied until the respective desired plating layers are obtained. The specific plating conditions will depend on the metal substrate to be used, plating solution composition, purpose, and the like. The conditions which are usually used for Ni-chromium plating can be selected as appropriate. For example, in the case where a semigloss nickel plating layer (5 to 15 μm), a tri-nickel plating layer (1 to 2 μm), and a gloss nickel plating layer (5 to 15 μm) are to be sequentially formed on an Fe substrate, it is preferable to control the temperature of the plating solution to be about 40 to 65°C , and the pH of the plating solution to be about 2 to 5. The plating time is preferably about 10 to 20 minutes for semigloss nickel plating as well as gloss nickel plating, and about 1 to 5 minutes for tri-nickel plating. Note that a strike nickel layer may be further provided between the underlying plating layer and the metal substrate.

[0100] Next, a chromium plating layer is formed on the metal substrate on which the underlying plating layer has been formed. As shown in FIG. 7, a chromium plating apparatus 20 includes a chromium plating trough 11 in which to perform chromium plating, a pump 12 for pumping up a plating solution which has been introduced to the chromium plating trough 11, a percolator 13 for removing impurities which are suspended in the plating solution, an adjustment valve 14 for adjusting the flow rate of the plating solution, and a flowmeter 15 for monitoring the flow rate of the plating solution. On the downstream end of the chromium plating apparatus 20, an ion exchange apparatus 16 for removing the metal ions (such as Fe) contained in the plating solution is provided. The chromium plating apparatus 20 and the ion exchange apparatus 16 are connected to each other via a metal tube (not shown).

[0101] The chromium plating trough 11 is filled with a trivalent chromium plating solution. As a trivalent chromium ion source, the plating solution contains basic chromium sulfate which converts to 30 to 40g/l of chromium.

[0102] In order for the amounts of boron and iron contained in the chromium plating layer to fall within the aforementioned ranges, it is necessary to ensure that the concentrations of boron and iron within the plating solution that is used fall within predetermined ranges. Specifically, the trivalent chromium plating solution has a boric acid content in a range from 1 to 5 g/l as converted to a boron amount, and an Fe content of 0.5 mg/l or less.

[0103] The boric acid content is reduced to about 1/15 to 5/6 as compared to the amount of boron that is added to a typical conventional trivalent chromium plating solution (about 6 to 15 g/l). In recent years, regulations on the amounts of boron to be discharged to the environment have been introduced. Using a plating solution with a low boron concentration also complies with such environmental regulations.

[0104] Moreover, a typical conventional trivalent chromium plating solution contains about 0.0001 to 0.0003 mass% of ferrous sulfate as an additive, in order to enhance the throwing power and the like of the plating layer. Therefore, when using a conventional trivalent chromium plating solution, the chromium plating layer contains about 2 to 20 mass% of Fe. However, it is preferable that the trivalent chromium plating solution to be used in the present invention does not contain such an additive, and the Fe content is restricted to 0.5 mg/l or less.

[0105] Boric acid is used to adjust pH and to allow the chromium plating layer to acquire a silver-gray color tone. Therefore, in order to reduce the boric acid amount and maintain appropriate pH, the trivalent chromium plating solution to be used in the present invention contains citric acid or a citrate compound, as converted to a citric acid amount in a range from 5 to 30 g/l. As citrate compounds, citrates such as potassium citrate or metal citrate compounds such as nickel citrate can be used. In order to obtain a chromium plating layer with good color tone, it is more preferable to use citric acid. The amount of citric acid to be added is preferably no less than 10 g/l and no more than 25 g/l, and more preferably no less than 20 g/l and no more than 25 g/l.

[0106] The chromium plating is to be carried out via electroplating. The chromium plating trough 11 is filled with the aforementioned trivalent chromium plating solution, and a metal substrate 17 which is to receive chromium plating is used as a cathode. Since chromium plating is to be performed while supplying chromium ions from the plating solution, an insoluble anode 18 which does not dissolve in a chromium plating solution is used as an anode.

[0107] Next, the DC power source 19 is connected between the electrodes, and power is supplied therefrom. The chromium ions contained in the chromium plating solution move toward the cathode side, i.e., the metal substrate 17, where the ions are reduced to metal Cr and deposit.

[0108] In order to form a chromium plating layer of 0.2 μm or more in a region which is to be heated to a temperature of 350˚C or above, the plating is preferably performed while placing the metal substrate in a position which will allow a chromium plating layer having a desired thickness to be formed. In particular, in the case where a metal substrate such as a curved exhaust pipe is to be plated, it is preferable to locate the metal substrate so that the distance between the electrode and the material to be plated (metal substrate) is as short as possible.

[0109] For example, as shown in FIG. 8(a), if the metal substrate 17 is arranged so that the distance between the convex portion 9a of the bent portion of the metal substrate 17 and the electrode 18 becomes smallest, a Cr layer can be efficiently formed at the convex portion 9a, which will be heated to a high temperature.

[0110] On the other hand, as shown in FIG. 8(b), if the metal substrate 17 is arranged so that a long distance exists between the convex portion 9a of the metal substrate 17 and the electrode 18, a chromium plating layer is likely to be formed at the concave portion opposite from the convex portion 9a, and not at the convex portion 9a itself, thus resulting in a poor plating efficiency.

[0111] Otherwise, by controlling the amount of charge (current $\times$ time) traveling through the electrode surface, current density, or the like, for example, the thickness of the chromium plating layer can be controlled to be within a predetermined range. In particular, the electrode positioning may be controlled, or an auxiliary electrode may be attached to control the current density or the like, for example, thus making it easier to form a predetermined chromium plating layer in regions which are to be heated to a temperature of 350˚C or above. In the specific controlling method, appropriate conditions may be selected according to the type and shape of the metal substrate which is used, the constitution of the plating solution, the thickness of the chromium plating layer, or the like. Especially in the case where no ferrous sulfate is contained in the plating solution, the throwing power of a plating layer will generally worsen, and therefore it is necessary to ensure a uniform current density by optimizing the electrode location, for example.

[0112] The boron contents in the chromium plating layer to be formed depends not only on the boron concentration in the plating solution but also on the temperature of the plating solution, plating time, stirring rate of the plating solution, etc., and in particular on the temperature of the plating solution. Generally speaking, the boron content in the chromium plating layer increases as the temperature of the plating solution increases. Therefore, in order to keep the boron amount in the chromium plating layer within the aforementioned range, it is preferable to control the temperature of the plating solution to be in a range from 25˚C to 30˚C.

[0113] In order to ensure that the iron content in the chromium plating layer falls in the aforementioned range, it is necessary to pay attention to the iron which elutes from the metal substrate into the plating solution. Moreover, even if the metal substrate does not include iron as its main component, Fe may inevitably gather at the chromium plating layer in some cases. As a result, even if ferrous sulfate is not added to the plating solution, the iron concentration within the plating solution may increase so that iron may be contained in the chromium plating layer.

[0114] In order to eliminate such possibilities, it is necessary to regularly monitor the iron concentration in the plating solution during plating, and remove the iron when the iron concentration reaches a predetermined value or more. The iron ions which stray into the plating solution are to be removed by using the ion exchange apparatus 16, which includes a cation exchange resin. The cation exchange resin to be used for the present invention may be any resin that permits easy exchange with divalent metal cations such as Fe, without any particular limitations.

[0115] The specific removal method may be as follows. First, during the plating, the plating solution is regularly pumped up from the plating trough 11 by using the pump 12, and suspended matter is removed by using the percolator 13. Next, the plating solution from which the suspended matter has been removed is introduced into the ion exchange apparatus 16, while adjusting the flow rate via the adjustment valve 14, and metal cations such as Fe ions are removed by using the cation exchange resin. The flow rate of the plating solution is monitored with the flowmeter 15. The plating solution which has been processed by the ion exchange apparatus 16 is regularly collected in order to check for Fe concentration. In order to reduce the Fe concentration within the chromium plating layer to 2 mass% or less as in the present invention, it is necessary to control the Fe concentration in the plating solution to be about 0.0001 mass% or less. Thus, removal by the ion exchange apparatus 16 is performed until the aforementioned range is satisfied.

[0116] The plating solution (recovered plating solution) from which Fe ions are thus removed exits the outlet of the ion exchange apparatus 16, and is led through the tube path 24, thus to be circulated to the plating trough 11. The recovered plating solution may be stored in an appropriate storage container (not shown), for example.

[0117] Note that a technique of removing metal cations within a plating solution by using the ion exchange apparatus 16 is specifically described in Patent Document 4, for example, and such a technique is applicable to the method of the present invention. Moreover, various alterations thereof have also been proposed (e.g., Patent Document 5), which are also applicable to the method of the present invention.

[0118] The chromium plating layer after the plating has a surface roughness (Ra) of about 1 μm or less, and preferably a surface roughness of 0.2μm or less. Therefore, after the plating, the chromium plating layer has sufficient luster, without the need to particularly finish up the surface.

3. Experimental example

(Experimental Example 1)

[0119] In this Experimental Example, the following experiment was performed in order to prove that stability of plating growth is ensured by setting the lower limit of the boron content in the chromium plating layer to be 0.05 mass%.

[0120] First, metal tubes composed of STKM were prepared, and a Ni plating layer composed of a semigloss Ni plating layer, a tri-Ni plating layer, and a gloss Ni plating layer was formed by the following method. The compositions of the plating solutions used for forming these plating layers are shown in Table 1. Note that the C and/or S contained in the tri-Ni plating solution was supplied from an additive other than a brightener.

[0121] Semigloss Ni plating layer (thickness: about 5 to 15 μm)
plating conditions: power was supplied at 10 to 12V (volts), 1800 to 2800A (amperes).
Tri-Ni plating layer (thickness: about 1 to 5 μm)
plating conditions: power was supplied at 3 to 3.5V (volts), 20 to 40A (amperes).
Gloss Ni plating layer (thickness: about 5 to 15 μm)
plating conditions: power was supplied at 10 to 12V (volts), 1800 to 2800A (amperes).

[0122]

[Table 1]

Component	Semigloss Nickel	Tri-Nickel	Gloss Nickel
Nickel Sulfate (g/l)	200-260	180-230	200-400
Nickel Chloride (g/l)	30-60	30-60	30-60
Boric Acid (g/l)	35-60	35-60	35-60
Brightener	Added	None	Added
Amounts of carbon and sulfur (%)	0.0001	0.1-0.2	0.05
pH	4-4.4	2-2.4	4-4.4

[0123] Next, by using a chromium plating apparatus having an ion exchange apparatus as shown in FIG. 6, a chromium plating layer was formed on the underlying plating layer (the chromium plating layer had a thickness of 0.3 μm). As the chromium plating solution, four types of trivalent chromium plating solutions as described in Table 2 were used (Nos. 1 to 4). The components of the trivalent chromium plating solutions of Sample 1 to Sample 4 were identical except for different ferrous sulfate and boric acid contents. Specifically, each of these trivalent chromium plating solutions contained citric acid, and ferrous sulfate was added in amounts of 0 (Sample 1), 2.5 mg/l (Sample 2), 5 mg/l (Sample 3), and 10 mg/l (Sample 4); or, as converted to Fe amounts, 0 (Sample 1), 0.05 mg/l (Sample 2), 0.1 mg/l (Sample 3), and 0.3 mg/l (Sample 4). On the other hand, boric acid was added in amounts of 5 g/l (Sample 1), 5 g/l (Sample 2), 30 g/l (Sample 2), and 60 g/l (Sample 3).

[0124]

[Table 2]

Component	Sample 1 (Present Invention)	Sample 2 (Present Invention)	Sample 3 (Comparative Example)	Sample 4 (Comparative Example)
Basic Chromium Sulfate $Cr(OH)SO_4$ (g/l)	95-115	95-115	95-115	95-115

(continued)

Component	Sample 1 (Present Invention)	Sample 2 (Present Invention)	Sample 3 (Comparative Example)	Sample 4 (Comparative Example)
Boric Acid H_3BO_4 (g/l)	5	5	30	60
Citric Acid*	30	30	30	30
Ammonium Formate $HCOONH_4$ (g/l)	200	200	200	200
Surfactant**(mg/l)	6.5	6.5	6.5	6.5
Ferrous Sulfate $FeSO_4 \cdot 7H_2O$ (mg/l)	0	2.5	5	10
(Note) *$HOOCCH_2C(OH)(COOH)CH_2COOH$ **Sodium Sulfosuccinate 2-Ethylhexyl Sodium Sulfate				

[0125] Note that, in order to adjust the boron content in the plating layer in various ranges, the temperature of the plating solution was varied in a range from about 25 to 60°C, and the current density was varied in a range from about 10 to 30A/dm^2, while also adjusting the air agitation amount of the plating solution.

[0126] In the case where the trivalent chromium plating solution of Sample 1 (Present Invention) was used, the Fe ions which strayed into the plating were removed by using an ion exchange apparatus having a cation exchange resin. Specifically, a plating solution was regularly fed to the ion exchange apparatus, and the Fe concentration within the plating solution was controlled to be within the range from 0 to 0.0001 mass%. As a result, in the case where the trivalent chromium plating solution of Sample 1 (Present Invention) was used, the Fe content in the chromium plating layer was 0.2 mass% at the most, when being measured along the thickness of the plating layer. On the other hand, in the case where the trivalent chromium plating solutions of Sample 2 to Sample 4 were used, the respective chromium plating layers had Fe contents (maximum values) of 2.0 mass%, 7.0 mass%, and 15.0 mass% because Fe ion removal with an ion exchange apparatus was not performed.

[0127] With respect to each sample, stability of plating growth was measured by the aforementioned method, and evaluations were made according to the following standards, based on the thickness of the chromium plating layer at each measurement site.

<Stability of Plating Growth>

[0128] Evaluation Standards (where ◎ to Δ correspond to Present Invention)
◎: chromium plating layer has a thickness in the range of no less than 0.25mm but less than 0.5mm.
○: chromium plating layer has a thickness in the range of no less than 0.20mm but less than 0.25.
Δ: chromium plating layer has a thickness in the range of no less than 0.05mm but less than 0.20mm.
× : chromium plating layer has a thickness less than 0.05mm.

[0129] The obtained results are shown in Table 3.

[0130]

[Table 3]

Sample No.	Concentration of Iron added to Plating Solution (mg/l)	Concentration of Iron in Plating Layer (mass %)	Boron Content in Chrome Plating Layer (mass %)				
			0	0.05	0.1	0.2	0.3
Sample 1	0	0.2		○	◎	◎	◎
Sample 2	2.5	2	×	○	◎	◎	◎
Sample 3	5	7.0	×	○	◎	◎	◎
Sample 4	10	15.0	×	○	◎	◎	◎

[0131] It can be seen from Table 3 that, when any of the trivalent chromium plating solutions of Sample 1 to Sample 4 is used, plating growth becomes considerably unstable in the case where no boron is contained in the chromium plating layer (zero content), but plating can stably grow in the case where plating conditions are set so that at least 0.05 mass% or more of boron is contained in the chromium plating layer. As far as stable plating growth is concerned, the boron content in the chromium plating layer is preferably as much as possible.
[0132] Thus, it has been proven that boron is an indispensable component for ensuring stability of plating growth, and that good plating characteristics cannot be obtained from merely adding citric acid instead of boric acid. This effect, i.e., stable growth of plating which is realized by the addition of boron, was similarly observed irrespective of the Fe content in the plating layer.
[0133] Next, in order to further investigate in the aforementioned effects of boron, chromium plating layers were formed in a manner similar to the aforementioned method by using the trivalent chromium plating solution of Sample 1, and their plating anticorrosiveness and plating abrasion resistance were measured according to the aforementioned method, based on the following standards.

<Plating Anticorrosiveness>

[0134] Evaluation Standards (where ◎ to Δ correspond to Present Invention)
◎: rating number is no less than 9.0.
○: rating number is no less than 8.0 but less than 9.0.
Δ: rating number is no less than 7.0 but less than 8.0.
×: rating number is less than 7.0.

<Plating Abrasion Resistance>

[0135] Evaluation Standards (where ◎ to Δ correspond to Present Invention)
◎: Vickers hardness is 500 Hv or more.
○ : Vickers hardness is no less than 450 Hv but less than 500 Hv.
Δ: Vickers hardness is no less than 350 Hv but less than 450 Hv.
×: Vickers hardness is less than 350 Hv.
[0136] The obtained results are shown in Table 4. Table 4 also shows results of plating growth stability.
[0137]

[Table 4]

Characteristics	Boron Content in Chrome Plating Layer (mass %)				
	0	0.05	0.1	0.2	0.3
Stability of Plating Growth	×	○	◎	◎	◎
Plating Anticorrosiveness	×	◎	◎	○	Δ
Plating Abrasion Resistance	×	◎	◎	○	Δ

[0138] It can be seen from Table 4 that plating anticorrosiveness and plating abrasion resistance are considerably degraded in the case where no boron is contained in the chromium plating layer (zero content), but these properties are improved in the case where plating conditions are set so that at least 0.05 mass% or more of boron is contained in the chromium plating layer. These results are similar to the aforementioned results of stability of plating growth. Thus, it can be seen that boron is an indispensable component not only for the enhancement of stability of plating growth but also for the enhancement of plating anticorrosiveness and plating abrasion resistance.
[0139] However, as shown in Table 4, plating anticorrosiveness and plating abrasion resistance are gradually degraded once the boron content in the chromium plating layer exceeds 0.1 mass%. These results differ from the aforementioned results of stability of plating growth.
[0140] From the above results, in order to improve the plating film-forming characteristics which are to be evaluated in a totalistic manner based on the three properties of plating growth stability, plating anticorrosiveness, and plating abrasion resistance, it is preferable to control the boron content in the chromium plating layer to be in the range from 0.05 to 0.3 mass%.

(Experimental Example 2)

[0141] In this Experimental Example, the following experiment was performed in order to prove that the color tone of a chromium plating layer immediately after plating is improved by controlling the boron content and Fe content in the chromium plating layer.
[0142] Specifically, four kinds of trivalent chromium plating solutions, i.e., Sample 1 to Sample 4 in Experimental Example 1, were used to form chromium plating layers in a manner similar to Experimental Example 1 described above.
[0143] With respect to each sample thus obtained, a color tone immediately after plating was measured by the following method, and evaluated based on the following standards.

<Color Tone Immediately After Plating>

[0144] By using a spectrometric color difference meter (color analyzer TC-1800MK-II (Tokyo Denshoku)), the L* value was measured according to the method described in CIE 1976. The color tone of a chromium plating layer which is obtained by using a hexavalent chromium plating solution is in a range from 70 to 80 in L* value. In this Experimental Example, it is regarded that a color tone similar to that of a chromium plating layer which is obtained from a hexavalent chromium plating solution has been obtained so long as the L* value is 68 or more.

Evaluation Standards:

[0145] ◎: A good color tone similar to that which is obtained by using hexavalent chromium is obtained.
(L* value = no less than 70 and no more than 80) ○: A color tone similar to that which is obtained by using hexavalent chromium is obtained, with a slightly lower metallic luster.
(L* value = no less than 68 but less than 70) Δ: A slightly blackish color tone is obtained.
(L* value = no less than 65 but less than 68) ×: A blackish color tone is obtained.
(L* value = less than 65)
[0146] These results are shown in Table 5.
[0147]

[Table 5]

Sample No.	Concentration of Iron in Plating Layer (mass %)	Boron Content in Chrome Plating Layer (mass %)							
		0.05	0.1	0.2	0.3	0.5	0.8	1.0	1.5
Sample 1	0.2	◎	◎	Δ	Δ	×	×	×	×
Sample 2	2	○	○	Δ	Δ	×	×	×	×
Sample 3	7.0	Δ	Δ	Δ	Δ	×	×	×	×
Sample 4	15.0	×	×	×	×	×	×	×	×

[0148] As is clear from Table 5, when the trivalent chromium plating solution of Sample 4 was used and the Fe content in the chromium plating layer was controlled to 15.0 mass%, a chromium plating layer with a blackish color tone was obtained, irrespective of the boron content in the chromium plating layer.
[0149] When the trivalent chromium plating solution of Sample 3 was used and the Fe content in the chromium plating layer was controlled to 7.0 mass%, a chromium plating layer with a slightly blackish color tone was obtained by controlling the boron amount to 0.3 mass% or less.
[0150] On the other hand, when the trivalent chromium plating solution of Sample 2 was used and the Fe content in the chromium plating layer was reduced to 2.0 mass%, a chromium plating layer with a slightly blackish color tone was obtained by controlling the boron amount to 0.3 mass% or less, and a chromium plating layer having substantially the same color tone as that of a chromium plating layer which is obtained from a hexavalent chromium plating solution was obtained by further controlling the boron amount to 0.1 mass% or less. Moreover, similar results were also obtained when the trivalent chromium plating solution of Sample 1 was used and the Fe content in the chromium plating layer was reduced to 0.2 mass%, with the boron amount being controlled to 0.3 mass% or less. By reducing the Fe content in the chromium plating layer to 0.2 mass% and controlling the boron amount to 0.1 mass% or less, a chromium plating layer having a color tone which is almost indistinguishable from that of a chromium plating layer which is obtained from a hexavalent chromium plating solution was obtained.
[0151] Accordingly, it will be seen that a trivalent chromium plating layer having a color tone similar to that obtained

by using hexavalent chromium can be obtained by reducing the Fe amount in the trivalent chromium plating layer to 2.0 mass% or less and reducing the boron amount to 0.1 mass% or less. Note that, so far as color tone is concerned, better characteristics are obtained as the Fe content and boron content in the chromium plating layer are smaller.

(Experimental Example 3)

[0152] In this Experimental Example, it was examined as to how cracks would occur before and after heating and how the color tone of a chromium plating layer would change depending on the thickness of the chromium plating layer.

[0153] Specifically, by using the trivalent chromium plating solution of Sample 1 in Experimental Example 1, chromium plating layers were formed in a manner similar to Experimental Example 1. The thickness of a chromium plating layer can be adjusted by appropriately controlling the plating time depending on the size of the plating material used, and the like. In this Experimental Example, plating time was varied in a range of 0.3 to 5 minutes, thus changing the thickness of the chromium plating layer from 0.1 to 1.5 μm.

[0154] With respect to each sample thus obtained, occurrence of cracks that are observed immediately after plating (before heating) was measured by the following method, and evaluated according to the following standards. Furthermore, according to the aforementioned method, the color tone of the chromium plating layer immediately after plating was measured and evaluated.

[0155] Next, each of the aforementioned samples was placed in an atmospheric furnace, and after being heated under the conditions of 400°C×8 hours, occurrence of cracks after heating was examined by the same measurement method and evaluation standards as those used when examining occurrence of cracks observed immediately after plating.

<Occurrence of Cracks>

[0156] Measurement method: By using an optical microscope (magnification: ×400), cracks occurring in the chromium plating layer surface (about 10 mm × 10 mm) were observed.

[0157] Evaluation Standards (◎ to Δ correspond to Present Invention):

◎: There are no cracks.

○: A few discontinuous cracks are observed.

Δ: Some slightly continuous cracks have occurred.

×: A large number of continuous cracks have occurred.

[0158] Occurrence of cracks is shown altogether in Table 6. Also, the color tone of each chromium plating layer immediately after plating is shown in Table 7.

[0159]

[Table 6]

Sample No.	Thickness of Chromium Plating Layer (μm)	Boron Content in Chrome Plating Layer (mass %)							
		0.05	0.1	0.2	0.3	0.5	0.8	1.0	1.5
Before Heating	0.1	◎	◎	◎	◎	◎	○	○	○
	0.3	◎	◎	◎	◎	◎	○	○	○
	0.5	◎	◎	○	○	Δ	×	×	×
	0.7	○	○	○	○	Δ	×	×	×
	1.5	×	×	×	×	×	×	×	×
After Heating	0.1	◎	◎	○	Δ	×	×	×	×
	0.3	◎	◎	○	Δ	×	×	×	×
	0.5	◎	◎	○	Δ	×	×	×	×
	0.7	◎	○	Δ	Δ	×	×	×	×
	1.5	×	×	×	×	×	×	×	×

[0160] As shown in Table 6, it can be seen that cracks are more likely to occur when the thickness of the chromium plating layer increases and the boron content in the chromium plating layer increases.

[0161] For example, the experimental results before heating (immediately after plating) indicate that hardly any cracks occurred while the chromium plating layer had a thickness in the range from 0.1 to 0.3μm, even if the boron content in the chromium plating layer was increased to 1.5 mass%. Cracks were more likely to occur as the thickness of the chromium plating layer increased to 0.5 μm or above, and when the chromium plating layer had a thickness of 1.5 μm, cracks occurred irrespective of the boron content in the chromium plating layer.

[0162] On the other hand, there was a tendency that cracks were more likely to occur in the case where a heat treatment was performed at 400 ˚C for 8 hours, as compared to before heating. Specifically, even if the thickness of the chromium plating layer was in the range from 0.1 to 0.7 μm, it was not possible to effectively prevent crack generation unless the boron content in the chromium plating layer was controlled to 0.05 to 0.3 mass%. An even more preferable boron content would be 0.05 to 0.2 mass%. Note that cracks were likely to occur when the thickness of the chromium plating layer exceeded 0.7 μm, and cracks occurred irrespective of the boron content in the chromium plating layer when the thickness of the chromium plating layer was 1.5μm.

[0163] It can be seen from these experimental results that crack generation before and after heating can be effectively prevented by controlling the thickness of the chromium plating layer to 0.7μm or less, and further controlling the boron content in the chromium plating layer to be within a range from 0.05 to 0.3 mass%.

[0164] Next, with respect to samples whose chromium plating layers had boron contents of 0.05 mass% and 0.1 mass%, the thickness of the chromium plating layer was varied in a range from 0.05 μm to 0.7 μm, and the degree of discoloration due to heating was evaluated.

<Thermal Discoloration>

[0165] Measurement method: By using a spectrometric color difference meter (color analyzer TC-1800MK-II (Tokyo Denshoku)), the L* value, a* value, and b* value were measured, before and after heating, according to the method described in CIE 1976. The values before heating are labeled as "L0* value", "a0* value", and "b0* value", whereas the values after heating are labeled as "L1* value", "a1* value", and "b1* value". Thus, a color difference ΔE* value after heating was measured as follows.

[0166]

[Equation 1]

$$\Delta E * value = \sqrt{(L_1 * value - L_0 * value)^2 + (a_1 * value - a_0 * value)^2 + (b_1 * value - b_0 * value)^2}$$

[0167] Evaluation Standards (where ◎ to Δ correspond to Present Invention):

◎: ΔE* value <1

○: 1≦ΔE* value <3

Δ: 3≦ΔE* value <4

×: 4≦ΔE* value

[0168]

[Table 7]

Boric Acid Content (mass%)	Thickness of Chromium Plating Layer (μm)									
	0.05	0.10	0.15	0.20	0.25	0.30	0.40	0.50	0.60	0.70
0.05	×	×	×	Δ	Δ	○	◎	◎	◎	◎
0.1	×	×	×	Δ	Δ	○	◎	◎	◎	◎

[0169] As is clear from Table 7, there was little change in color tone before and after heating when the thickness (μm) of the chromium plating layer was 0.2μm or more, and the color tone almost never changed when the thickness (μm) of the chromium plating layer was 0.3μm or more.

INDUSTRIAL APPLICABILITY

[0170] The present invention is broadly applicable to a vehicle having an engine (e.g., a motorcycle or an all-terrain four-wheeled vehicle) and a transportation apparatus having an engine (e.g., a ship or an airplane).

Claims

1. An engine part comprising: a metal substrate; a chromium plating layer covering at least a portion of a surface of the metal substrate, the chromium plating layer being formed from a trivalent chromium plating solution, wherein, the chromium plating layer includes a boron content of no less than 0.05 mass% and no more than 0.3 mass%, and the chromium plating layer has a thickness or 0.7 μm or less.

2. The engine part of claim 1, wherein the boron content in the chromium plating layer is no less than 0.05 mass% and no more than 0.1 mass%.

3. The engine part of claim 2, wherein the chromium plating layer includes an iron content of 2 mass% or less.

4. The engine part of claim 3, wherein the chromium plating layer covers a region of the metal substrate surface that is heated to a temperature of 350˚C or more.

5. The engine part of claim 4, further comprising an underlying plating layer provided between the metal substrate surface and the chromium plating layer, wherein,
   the chromium plating layer has a thickness of no less than 0.2 μm and no more than 0.7 μm in the region that is heated to a temperature of 350˚C or more.

6. The engine part of claim 5, wherein the underlying plating layer includes at least one of C and S.

7. The engine part of claim 6, wherein the underlying plating layer further includes Ni.

8. The engine part of claim 5, wherein the underlying plating layer is formed of a metal having a hardness lower than that of the Cr composing the chromium plating layer.

9. The engine part of claim 5, wherein the underlying plating layer is formed from Ni plating.

10. The engine part of any of claims 3 to 9, wherein the chromium plating layer has a color tone such that an L* value measured according to CIE (Commission Internationale de l'Eclairage) 1976 is in a range of no less than 68 and no more than 80.

11. The engine part of any of claims 5 to 10, wherein the metal substrate is composed of a material containing Fe, Al, Zn, or Mg as a main component.

12. The engine part of any of claims 1 to 11, wherein the metal substrate is a metal tube defining a passage through which an exhaust gas from an engine travels.

13. An engine comprising the engine part of any of claims 1 to 11.

14. A transportation apparatus comprising the engine part of claim 12.

15. A transportation apparatus comprising the engine of claim 13.

FIG. 1

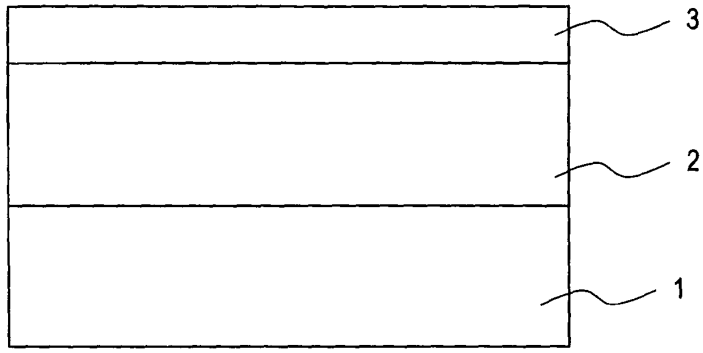
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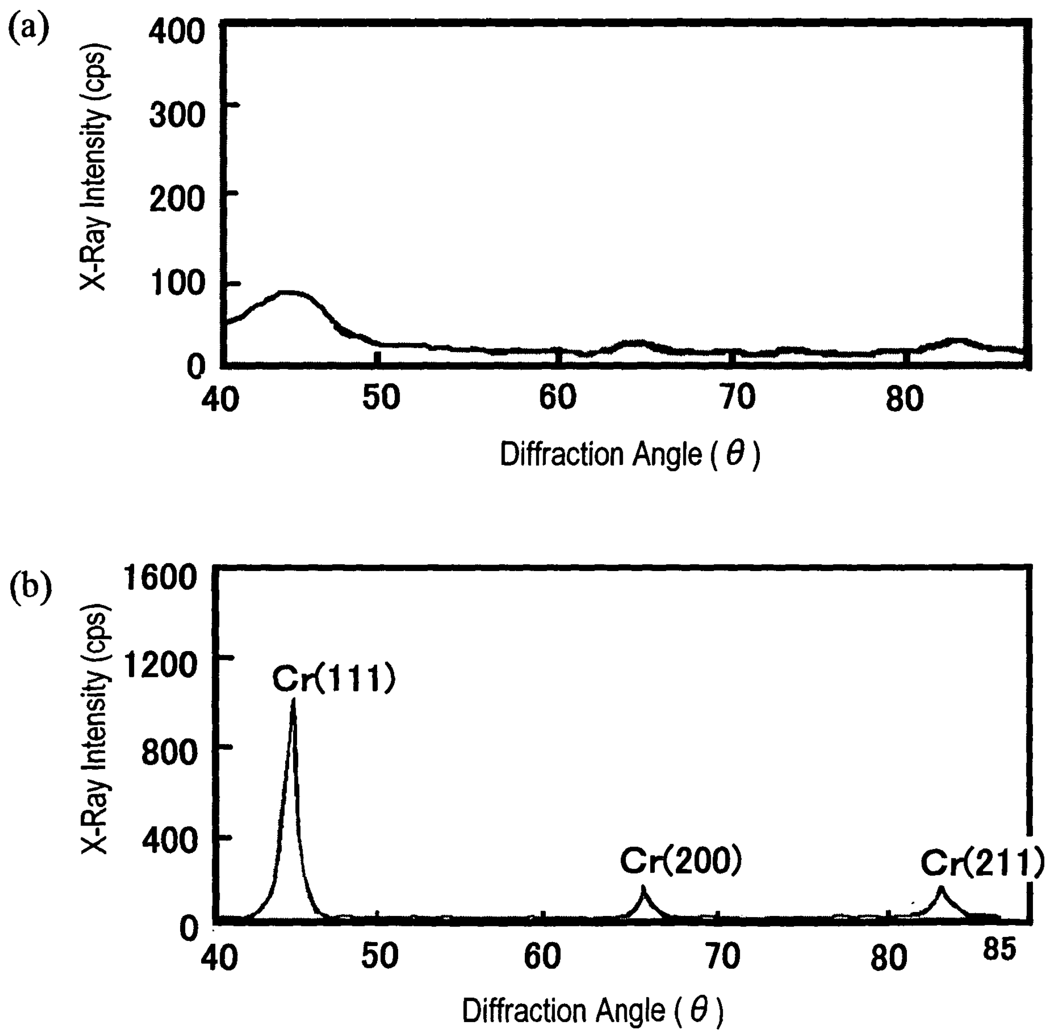
FIG. 2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300
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Diffraction Angle (θ)
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X-Ray Intensity (cps)
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1200
800
400
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Cr(200)
Cr(211)
40
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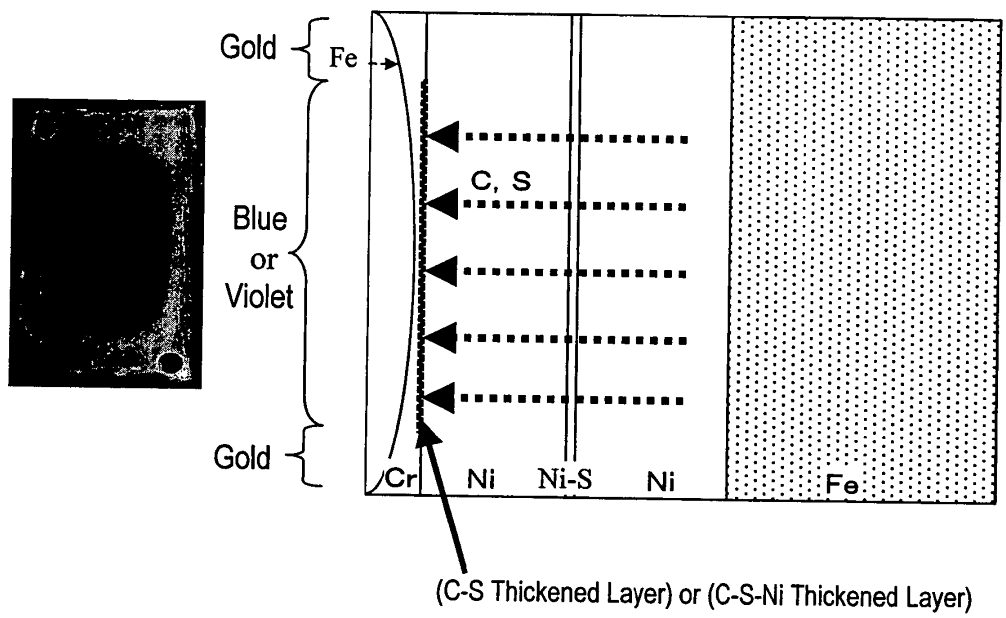
70
80
85
Diffraction Angle (θ)

FIG.3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Blue
or
Violet
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Cr
Ni
Ni-S
Ni
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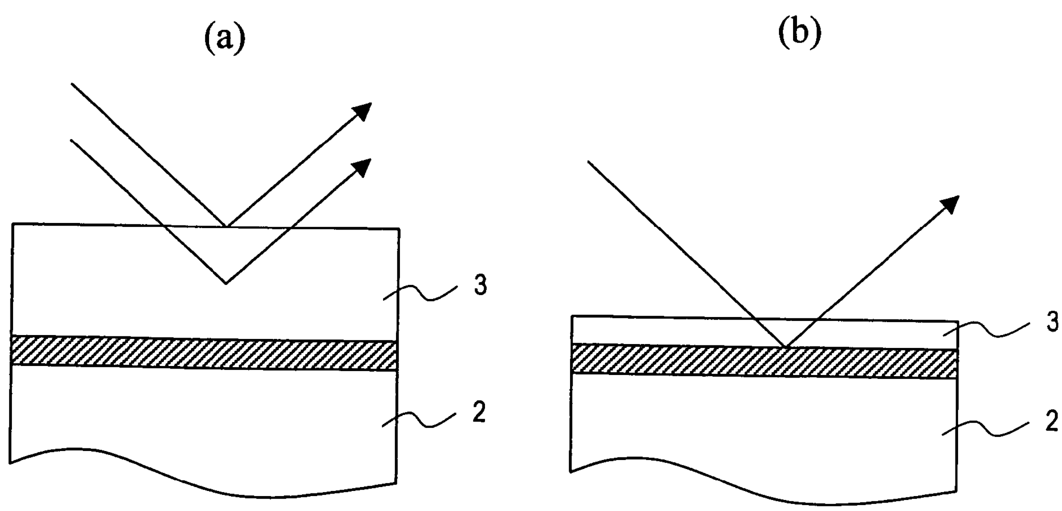
FIG.4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(b)
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FIG.5

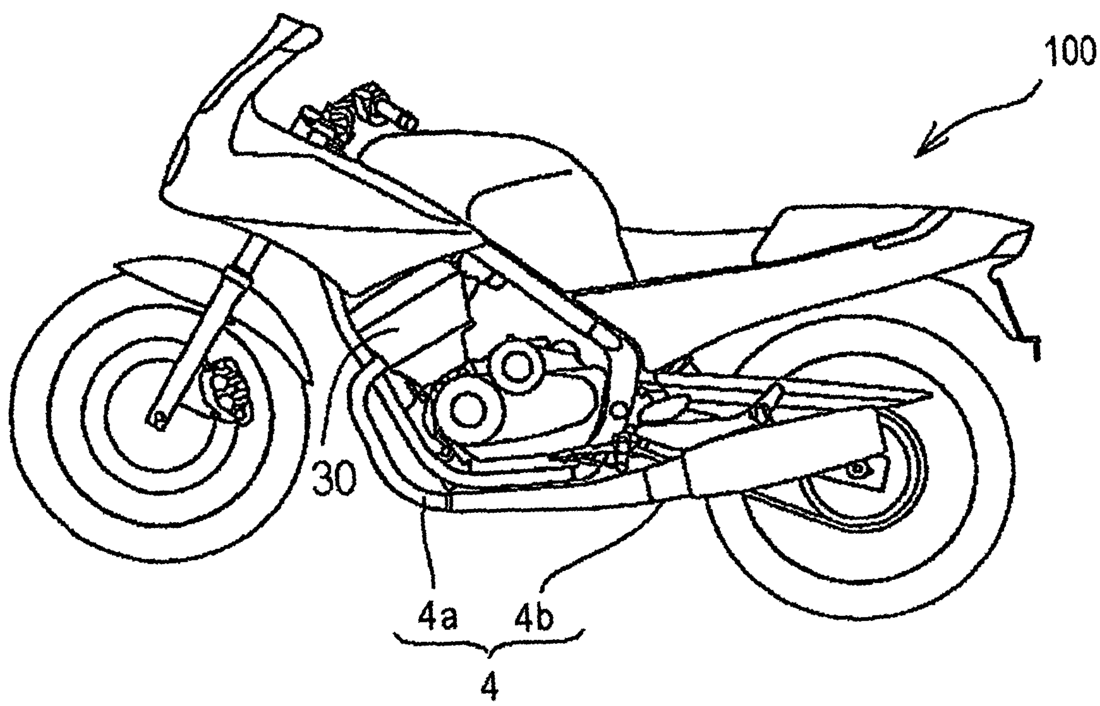


FIG.6

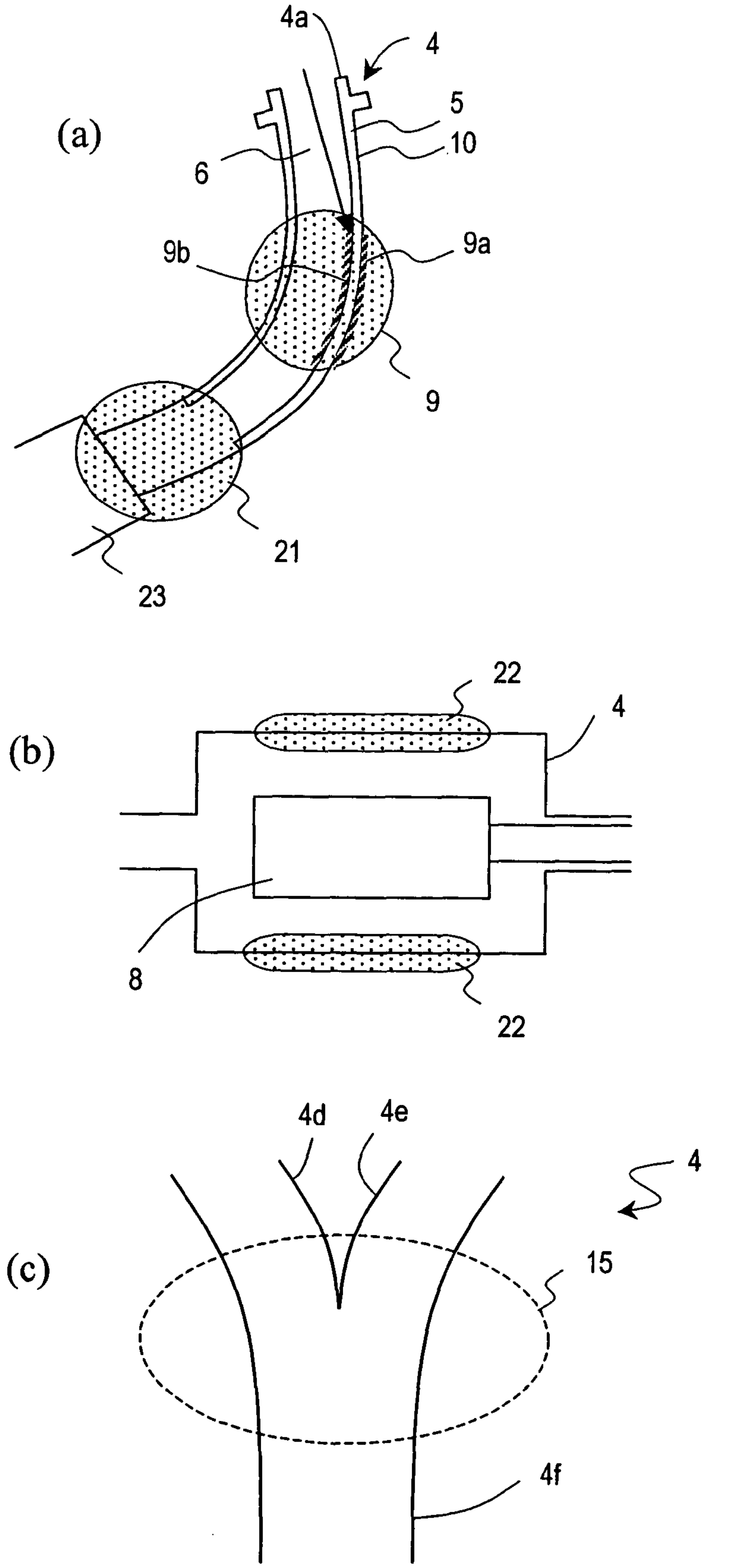


FIG. 7

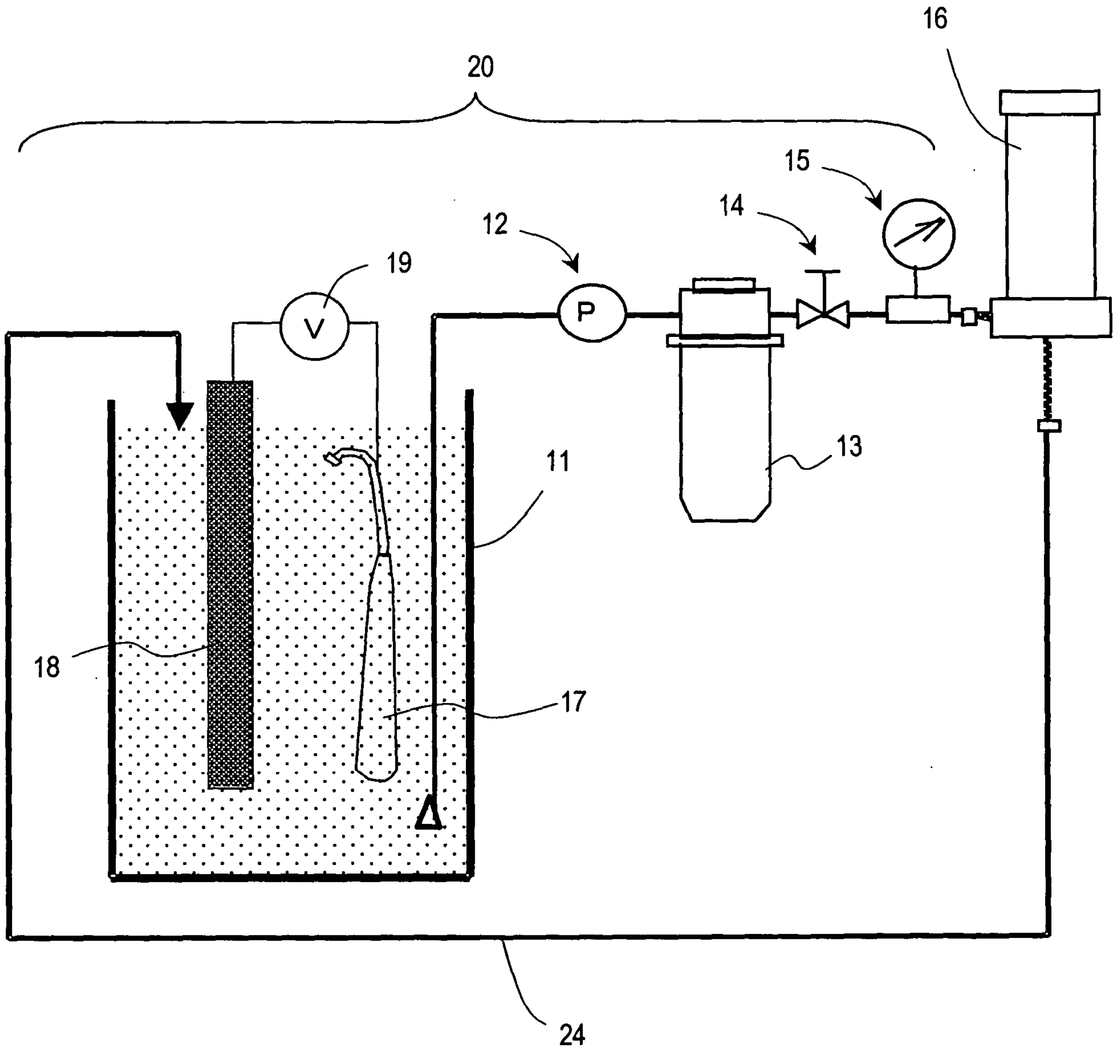


FIG.8

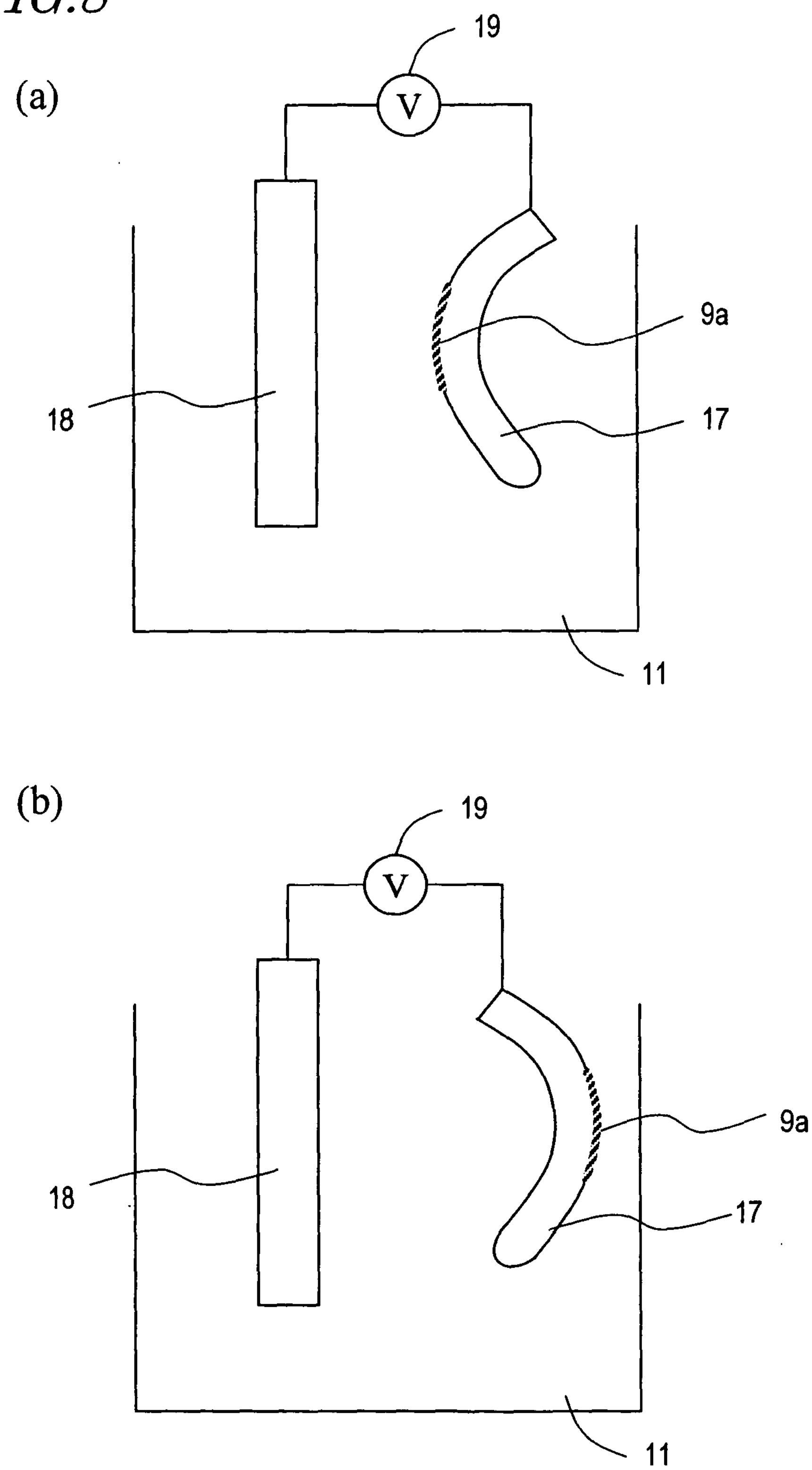
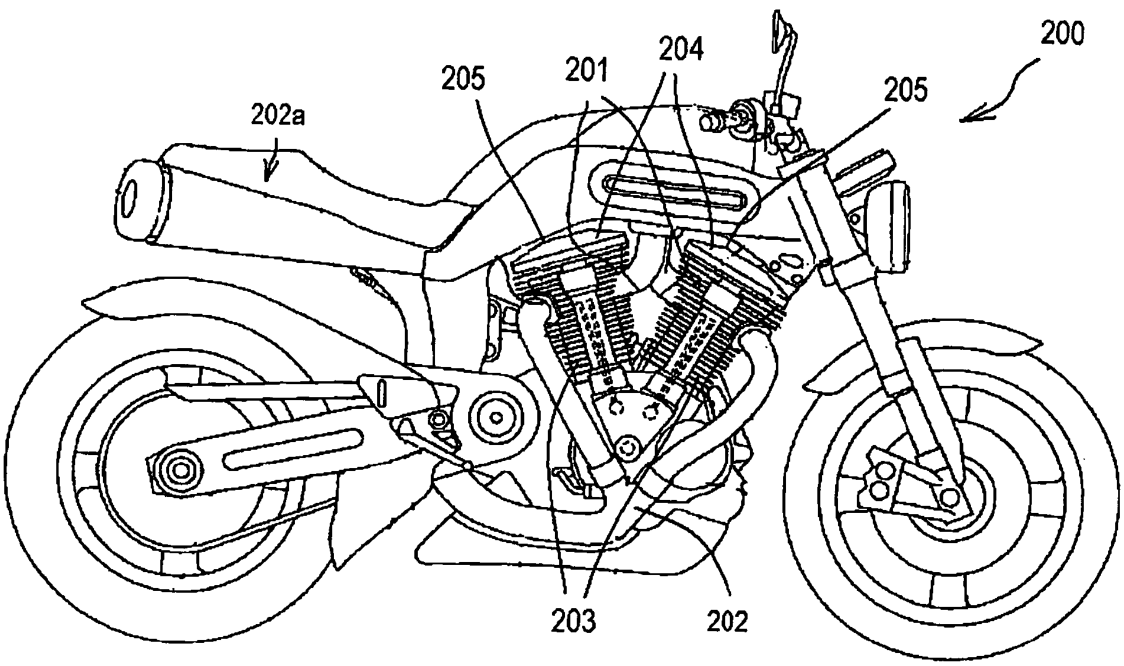


FIG.9



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/019037

A. CLASSIFICATION OF SUBJECT MATTER

C25D7/00(2006.01), ***F02F1/24***(2006.01), ***F02F1/00***(2006.01), ***F01N7/16***(2006.01),
C25D3/06(2006.01), ***C25D5/14***(2006.01), ***C25D7/04***(2006.01)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25D3/06, C25D5/14, C25D7/00, C25D7/04, F01N7/16, F02F1/00, F02F1/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2006
Kokai Jitsuyo Shinan Koho	1971-2006	Toroku Jitsuyo Shinan Koho	1994-2006

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2002-285375 A (Chinichi Kurafuto Kabushiki Kaisha), 03 October, 2002 (03.10.02), Par. No. [0022] (Family: none)	1-15
Y	JP 2002-371843 A (Yamaha Motor Co., Ltd.), 26 December, 2002 (26.12.02), Full text (Family: none)	1-15
A	JP 2003-171799 A (Tokico Ltd.), 20 June, 2003 (20.06.03), (Family: none)	1-15

☒ Further documents are listed in the continuation of Box C.　　☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 January, 2006 (04.01.06)	17 January, 2006 (17.01.06)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/019037

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 9-209199 A (The Nippon Chemical Industrial Co., Ltd.), 12 August, 1997 (12.08.97), (Family: none)	1-15
A	JP 58-153795 A (M & T Chemicals Inc.), 12 September, 1983 (12.09.83), & EP 88192 A	1-15

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

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- JP 9228069 A **[0010]**