

OPINION UNDER SECTION 74A

Patent	GB 2459372 B
Proprietor(s)	Zircotec IP Limited
Exclusive Licensee	
Requester	Gill Jennings & Every LLP
Observer(s)	
Date Opinion issued	30 July 2014

The request

1. The comptroller has been requested to issue an opinion as to whether claims 1-96 of GB 2459372 B ("the patent") are invalid under section 74A(1)(b) of the Patents Act 1977 by virtue of the lack of novelty or inventive step in light of the documents D1-D5 provided:

D1: US 2002/059727 A1

D2: Handbook of Thermal Spray Technology, ASM International, Second printing issued June 2005. ISBN 0871707950.

D3: WO 01/46324 A2

D4: US 2007/0102992

D5: "Plasma sprayed biocompatible coatings on PEEK implants", Beauvais et al, p371-376, Thermal Spray 2007: Global Coating Solutions, May 14-16, 2007, Beijing, People's Republic of China: proceedings of the 2007 International Thermal Spray Conference.

D6: A D6 is referred to in Annex 1, but no such document has been provided.

Observations

2. Observations on behalf of the proprietor were received from Withers & Rogers LLP on 13 June 2014 and observations in reply were received on behalf of Gill Jennings & Every LLP ("the requester") on 24 June 2014.

3. The proprietor argues in their observations that the requester has alleged lack of novelty of independent claims 1 and 44, but has not alleged that the independent claims lack an inventive step, and that thus under Rule 93 no opinion has been sought.

Rule 93 states:

Request for an opinion under section 74A

(1) A request must be made on Patents Form 17 and must be accompanied by a copy and a statement setting out fully—

(a) the question upon which an opinion is sought;

(b) the requester's submissions on that question; and

(c) any matters of fact which are requested to be taken into account.

...

4. As the requester points out in their observations in reply, the first paragraph of the initial request of 1 May 2014 states "We request an opinion on the validity of all claims" and "It is submitted that each of these claims lack novelty or inventive step...". As a result I am content that an opinion on validity in terms of both novelty and inventive step has been requested. Furthermore Annex 1 provided with the initial request sets out, albeit with very minimal explanation, the basis for novelty or inventive step arguments against all the claims in terms of the documents cited and, where appropriate, an indication of relevant passages of text. As a consequence I do not believe that this situation corresponds with that present in Opinion 15/08 where the limit of the inventive step argument was the statement "it also seems likely that any two of the documents combined render all of the claims of the present Patent obvious". Thus I am in a position to consider both the novelty and inventiveness of the claims.
5. Before going on to consider the patent and its validity I will now consider the appropriateness of allowing the arguments based on D3 for inventive step purposes.
6. Section 74A(3) of the Patents Act 1977 states:

The comptroller shall issue an opinion if requested to do so under subsection (1) above, but shall not do so –

 - (a) ..., or*
 - (b) if for any reason he considers it inappropriate in all the circumstances to do so.*
7. As the requester notes, D3 was considered pre-grant. However it was only considered on its own and in combination with other documents not now being utilised. As a consequence I am happy to consider this document in combination with the documents cited in the request, and do not consider it "inappropriate" in this situation. I will not, and indeed it has not been requested that I should, consider this document on its own.

The Patent

8. The patent was filed on 21 April 2009 with an earliest priority date of 21 April 2008, and published on 28 October 2009. It was granted on 6 March 2013 and remains in force.
9. The patent relates to a method of coating a substrate of organic material with a high melting point layer by first thermally spraying the substrate with a metal coating material before subsequently coating with the high melting point material e.g. a ceramic material. The patent also relates to articles, for example a bicycle wheel, medical implant or golf club head, which has a ceramic layer that is arranged on the surface of a thermally sprayed metal bond layer, where the e.g. ceramic coating material has a melting point which is higher than that of the metal bond layer and has a level of porosity greater than 5%.
10. The patent has ninety six claims and two independent claims, claims 1 and 44. Claim 1 reads as follows:

An article, the article including a substrate, at least a surface of the substrate being made of or containing an organic material, and a thermal sprayed first layer of coating material on the surface, and a further layer on the first layer, the coating material of the first layer being wholly or principally metal material, the first layer being less than 200 micrometres in thickness and the further layer being of a material with a higher melting point than the coating material of the first layer, wherein the level of porosity in the further layer is greater than 5%.

Claim 44 reads as follows:

A method of coating a substrate surface made of or containing an organic material, the method comprising thermal spraying the surface with a first layer of coating material to a thickness of less than 200 micrometres and depositing a further layer on the first layer, the coating material of the first layer being wholly or principally metal material, the further layer being of a material with a higher melting point than the coating material of the first layer, wherein the level of porosity in the further layer is greater than 5%.

The Law

11. Section 1(1) of the Act reads:

A patent may be granted only for an invention in respect of the following conditions are satisfied, that is to say –
(a) the invention is new;
(b) it involves an inventive step...

Validity

12. Given that all of the claims relate to the same inventive concept, I shall concentrate on the independent claims 1 and 44, and will only consider the validity of the dependent claims if I find that claims 1 and 44 are invalid for want of novelty or inventiveness in view of the documents and arguments put before me.
13. I do not believe that the person skilled in the art, required by the usual purposive approach to claim construction as described in *Kirin-Amgen and others v Hoechst Marion Roussel Limited and others* [2005] RPC 9, would have any difficulty in understanding claims 1 and 44, and neither party has offered any submissions in relation to the interpretation of any of the claim wording as such. As a result I need merely to determine whether the claims are novel and inventive in light of the documents referred to in the request.

Novelty of claims 1 and 44

14. The requester argues that claim 1 is not novel given the disclosure of D1 particularly the passage at paragraphs [0027] and [0028]. This document discloses an embodiment of a roll for a paper making machine comprising a composite fibre shell with a first thermally sprayed metal bond coat less than 200 micrometres thick and a further ceramic layer sprayed on top of the bond coat. This much does not seem to be at issue; however the proprietor disputes that the document provides proof both of the melt temperature of the ceramic and of the level of porosity of the further layer required and suggests the onus is on the requester to provide it.
15. I do not agree with this argument. There seems to me to be no requirement that the requester should prove either of these values as such. Instead the requester needs to satisfy me on the balance of probabilities that the disclosure of D1 destroys the novelty of claim 1, i.e. that on the balance of probabilities both the melt temperature of the ceramic disclosed in D1 is higher than that of the disclosed metal layer and that the level of porosity is greater than 5%.
16. In addition, the proprietor also states that no new evidence can be submitted in response to their observations, and thus the lack of novelty of claims 1 (and 44) has not been proven (and by implication must remain so). By their reference to new evidence, I take them to be referring to Rule 96 which states:

...

(4) A person to whom observations are sent under paragraph (3) may, during the period of two weeks beginning immediately after the end of the relevant period, file observations confined strictly to matters in reply.

...

17. I agree that, as the proprietor notes, the requester does not provide the phase diagram or the molar percentage calculation used to establish the melting temperature of $\text{Al}_2\text{O}_3/\text{TiO}_2$ in their request. However where the melting temperature given has been derived from is apparent and the requester's willingness to provide

the details is stated in the initial request. Thus provision of these details (i.e. the phase diagram and the actual calculation) does not introduce a new argument which might disadvantage the proprietor. Thus I am content that the observations in reply have been confined to “matters in reply” and will consider the information substantiating the requester’s calculated melting temperature for the ceramic material.

18. The calculated melt temperature of the $\text{Al}_2\text{O}_3/\text{TiO}_2$ provided (1840 °C) is considerably higher than the nickel/chrome melt temperature of 1430 °C provided and thus this satisfies the requirement that “the further layer” should be “of a material with a higher melting point than the coating material of the first layer”. The level of porosity disclosed in D1 is a little more problematic. Not only does the disclosed range of 4-6% cover porosities both below and above the “greater than 5%” required in claim 1 of the patent, but also the current case law in relation to disclosures of ranges is rather unclear. In *Union Carbide Corp v BP Chemicals Ltd* [1998] RPC 1 (at page 15), it was held that a prior disclosure of a range should normally be regarded as disclosing each and every part of that range.
19. However, in the context of Markush claims Jacob LJ has since stated in *Dr Reddy’s Laboratories (UK) Ltd v Eli Lilly & Co Ltd* [2010] RPC 9 that “logic dictates rejection of the argument that a disclosure of a large class is a disclosure of each and every member of it” (I note that the requester suggests that the end points of the range should be treated as having been disclosed for novelty purposes; this is consistent with the practice outlined in the EPO examination guidelines, but is not UK case law).
20. In this situation the range is small (and thus the class is not large) and so I am happy to conclude that the required porosity is specifically disclosed in this instance. Furthermore if I am wrong then the claim lacks inventiveness as I consider that preparation of a ceramic layer with the requisite porosity from this small range would be within the ambit of the skilled worker.
21. Independent claim 44 shares most of its essential features with claim 1 in that it relates to a method of coating a substrate rather than the article including a substrate coated in the fashion defined. As a result, I agree with the requester and consider claim 44 is also not novel on the basis of D1, albeit with the same caveat as for claim 1.

Novelty and inventiveness of the dependent claims

22. I have noted above that Annex 1 provided by the requester sets out the basis for validity objections against the dependent claims in fairly perfunctory fashion. This being the case, I will first highlight the dependent claims (all the claims are reproduced in the annex below) that I consider clearly lack novelty on the basis of D1 and then concentrate on those dependent claims which the proprietor appears to deem important given that arguments were presented in relation to them (claims 12, 31-43, 62, 63 and 79-90).
23. I consider that claims 2-3, 8-11, 13, 16-19, 45, 47, 49-58, 64-67 and 69-71 clearly lack novelty as the requisite features are present in the disclosure of D1 at paragraphs [0026]-[0028].

24. In response to the requester's apparent contention that claims 12, 62 and 63 lack novelty in view of D1, the proprietor questions the disclosure of D1 as at paragraph [0028] it states:

"In the embodiment shown, ceramic layer 20 is sprayed on to carbon fiber shell 18 at a temperature of less than about 200 °F, and preferably at about a temperature of about 175 °F. Ceramic layer 20 is formed using a plasma spray device which applies a ceramic powder..."

and thus the proprietor argues that the ceramic layer cannot be thermally sprayed at these temperatures, let alone plasma sprayed, and as a result the reference to "plasma" must be an obvious mistake. The requester's observations in reply suggest that the temperatures referred to are in fact the surface temperature of the substrate not the temperature of the plasma. I note that the proprietor does not question the use of plasma spraying in relation to the metal bond coat layer in D1. D1 paragraph [0029] includes the statement that "An example of a commercially available plasma spray device which is suitable for applying the bond coat, ceramic layer 20 and/or PTFE layer 22 is sold by Sulzer Metco, Inc...". On the basis of this statement I can see no reason to suppose that a plasma spray device is used for the bond coat alone and thus find the requester's argument more persuasive. Therefore I consider claims 12, 62 and 63 to also lack novelty.

25. The requester appears to assert in Annex 1 that claims 31-43 and 79-90 relating to particular articles (a bicycle wheel, a golf club head and a medical implant) would be obvious on the basis of D1 in combination with D4, D5 or the common general knowledge (in relation to golf clubs as no D6 was provided) respectively. The proprietor argues that, as D1 is entitled "Roll for Paper Making Machine" and that the whole document is concerned with forming this cylindrical item, this document is only suitable for teaching how to coat cylindrical items. As none of the specifically claimed articles in the patent are cylindrical, the person skilled in the art would not seek to use the process of D1 to coat them. In response, the requester argues that it is well known in the art to take account of article shape and that such adaptation is standard practice in the art.
26. Although not used by either party in their submissions, I must follow the *Pozzoli* approach (*Pozzoli SPA v BDMO SA* [2007] EWCA Civ 588) when deciding matters of obviousness:

(1)(a) *Identify the notional "person skilled in the art"*

In this context I believe the appropriate person to be one skilled in the design and manufacture of coated products.

(1)(b) *Identify the relevant common general knowledge of that person;*

This skilled person would be familiar with substrate preparation, coating processes, particularly thermal (including plasma) coating processes, and suitable precursors for these processes.

(2) *Identify the inventive concept of the claim in question or if that cannot readily be done, construe it;*

I identify the inventive concept as the thermal spraying of a first metal-comprising layer onto at least part of a bicycle wheel, a golf club head or a medical implant prior to depositing a further layer on the first layer, the further layer being of a material with a higher melting point than the coating material of the first layer, wherein the level of porosity in the further layer is greater than 5%.

(3) Identify what, if any, differences exist between the matter cited as forming part of the “state of the art” and the inventive concept of the claim or the claim as construed;

Both D4 and D5 disclose plasma spraying of articles with ceramic material. Thus having assumed the mantle of the skilled worker, the difference between the matter cited and the inventive concept appears to me to be the initial application of a thermally sprayed metal layer to the organic material.

(4) Viewed without any knowledge of the alleged invention as claimed, do those differences constitute steps which would have been obvious?

In considering whether this extra step would then be obvious to the skilled worker, the important question is whether the skilled worker wishing to prepare one of the particular coated products claimed would look to the method of D1 to achieve that. I do not consider that the skilled worker would. As the proprietor has noted, D1 is not concerned with coating in general, but specifically with preparing a roll for a paper-making machine. To this end the document aims to provide what is described at paragraph 0006 as a “roll for use in a paper-making machine which has a low inertia, as well as good wear and release properties”. I can find no suggestion in this document that the particular coating method would be useful in other contexts and the requester has provided me with no arguments as to why the method of D1 should be combined with D4, D5 or the common general knowledge. Indeed both D4 and D5 appear to suggest that direct coating of ceramic onto substrates made of organic material is entirely possible with no need for an extra layer between the two. As a result I consider that claims 31-43 and 79-90 do possess an inventive step.

27. Furthermore I consider that the remaining claims (4-7, 14-15, 20-30, 46, 48, 59-61, 68, 72-78 and 91-96) all clearly lack an inventive step on the basis of either the passages presented by the requester in D1-D3 or the common general knowledge.

Conclusion

28. I am therefore of the opinion that claims 1-3, 8-13, 16-19, 44-45, 47, 49-58, 62-67 and 69-71 of GB 2459372 B lack novelty as a result of the disclosure of D1 and that claims 4-7, 14-15, 20-30, 46, 48, 59-61, 68, 72-78 and 91-96 lack an inventive step on the basis of the disclosures of documents D1-D3. However, I consider claims 31-43 and 79-90 to be both novel and inventive.

Application for review

29. Under section 74B and rule 98, the proprietor may, within three months of the date of issue of this opinion, apply to the comptroller for a review of the opinion.

Dr Simon Grand

Examiner

NOTE

This opinion is not based on the outcome of fully litigated proceedings. Rather, it is based on whatever material the persons requesting the opinion and filing observations have chosen to put before the Office.

Annex – Claims for GB 2459372 B

1. An article, the article including a substrate, at least a surface of the substrate being made of or containing an organic material, and a thermal sprayed first layer of coating material on the surface, and a further layer on the first layer, the coating material of the first layer being wholly or principally metal material, the first layer being less than 200 micrometres in thickness and the further layer being of a material with a higher melting point than the coating material of the first layer, wherein the level of porosity in the further layer is greater than 5%.
2. An article according to claim 1, wherein the surface of the article is made of a composite material including a matrix made of plastics material.
3. An article according to claim 2, wherein the surface is made of carbon fibre composite material.
4. An article according to claim 1, 2 or 3 wherein the coating material of the first layer has a melting temperature of no more than 1200 °C.
5. An article according to claim 4, wherein the coating material of the first layer has a melting temperature under 700 °C.
6. An article according any preceding claim, wherein the coating material includes one or more of tin, copper, aluminium, silver, gold, lead and zinc.
7. An article according to claim 6, wherein the coating material is copper or aluminium or a copper aluminium alloy.
8. An article according to any preceding claim, wherein the first layer is up to 150 micrometres in thickness.
9. An article according to any preceding claim, wherein the first layer is up to 100 micrometres in thickness.
10. An article as claimed in any preceding claim, wherein the first layer is at least 2 micrometres thick.
11. An article according to any preceding claim, wherein the first layer covers the whole of the said surface of the article.
12. An article according to any preceding claim, wherein the further layer is a thermally sprayed layer.
13. An article, as claimed in any preceding claim, wherein the first layer is incorporated in the organic material of the substrate.

14. An article according to any preceding claim, wherein the first layer of coating material is a powder.
15. An article according to any preceding claim, wherein the first layer of coating material is a foil.
16. An article according to any preceding claim, wherein the further layer is made wholly or principally of ceramic or metal or ceramic and metal.
17. An article according to any preceding claim, wherein the further layer is wholly or principally made of ceramic material.
18. An article according to any preceding claim, wherein the further layer comprises at least 50% of at least one of zirconia, titania or alumina.
19. An article according to claim 18, wherein, the further layer comprises wholly or principally at least one of zirconia, titania, or alumina.
20. An article as claimed in claim 18 or claim 19, wherein the further layer also includes at least one of yttria and magnesia.
21. An article according to any preceding claim, wherein the level of porosity in the further layer is at least 15%.
22. An article according to any preceding claim, wherein the article includes at least one additional layer on the further layer.
23. An article according to claim 22, wherein the or each additional layer is a thermal sprayed layer.
24. An article according to claim 22 or claim 23, wherein the or at least one additional layer is made principally or wholly of ceramic or metal or ceramic and metal.
25. An article as claimed in any preceding claim, wherein the further layer is at least as thick as the first layer.
26. An article as claimed in any preceding claim, wherein the further layer is thicker than the first layer.
27. An article as claimed in any preceding claim, wherein the further layer is at least 100 micrometres thick.
28. An article as claimed in any preceding claim, wherein the further layer is at least 150 micrometres thick.
29. An article as claimed in any preceding claim, wherein the further layer is not greater than 300 micrometres thick.
30. An article as claimed in any preceding claim, wherein the further layer is not greater than 250 micrometres thick.

31. An article according to any preceding claim, wherein the article is a bicycle wheel and the layers are on the braking area of the rim of the wheel.

32. An article as claimed in claim 31, wherein the bicycle wheel includes a rim for a bicycle tyre, the rim including an outer surface wholly or principally of carbon fibre composite material, the wheel including on the outer surface of the rim a first layer of coating material and a further layer, the further layer being wholly or principally of ceramic or metal or ceramic and metal and forming a braking surface to be contacted by a brake block.

33. An article according to claim 32, wherein the further layer is a layer wholly or principally of ceramic.

34. An article according to claim 33, wherein the further layer is at least 50% titanium dioxide.

35. An article according to any of claims 32 to 34, wherein the further layer is a thermal sprayed layer of material with a higher melting point than the melting point of the material of the first layer.

36. An article according to any of claims 32 to 35, wherein the bicycle wheel is wholly or principally of carbon fibre composite material.

37. An article as claimed in any of claims 1 to 30, wherein the article is a golf club and the layers are on at least one of the striking face and ground engage face of the golf club.

38. An article according to claim 37, wherein the head of the golf club is wholly or principally of carbon fibre composite material, and the further layer is wholly or principally molybdenum or tungsten.

39. An article according to any of claims 1 to 30, wherein the article is a medical implant.

40. An article according to claim 39, wherein the article is a bone or tooth implant.

41. An article according to claim 35 or claim 36, wherein the first layer is wholly or principally of silver.

42. An article according to claim 39, 40 or 41, wherein the further layer is wholly or principally of titanium.

43. An article according to any of claims 39 to 42, wherein there is an additional layer wholly or principally of hydroxyapatite.

44. A method of coating a substrate surface made of or containing an organic material, the method comprising thermal spraying the surface with a first layer of coating material to a thickness of less than 200 micrometres and depositing a further

layer on the first layer, the coating material of the first layer being wholly or principally metal material, the further layer being of a material with a higher melting point than the coating material of the first layer, wherein the level of porosity in the further layer is greater than 5%.

45. A method according to claim 44, wherein the first layer of coating material is plasma sprayed onto the surface.

46. A method according to claim 45, wherein the first layer of coating material is plasma sprayed in nitrogen.

47. A method according to claim 44, claim 45, or claim 46, wherein the method includes chemical modification of the surface prior to thermal spraying of the first layer to promote adhesion or reduce substrate outgassing.

48. A method according to any of claims 44 to 47, wherein the method includes temperature treatment of the surface prior to thermal spraying to reduce substrate outgassing.

49. A method according to any of claims 44 to 48, wherein the method includes roughening the substrate surface prior to thermal spraying thereon.

50. A method according to any of claims 44 to 49, wherein the substrate surface is made of plastics material or a composite material including a matrix made of a plastics material.

51. A method according to claim 50, wherein the surface is made of carbon fibre composite material.

52. A method according to any of claims 44 to 51, wherein the coating material includes one or more of tin, copper, aluminium, silver, gold, lead and zinc.

53. A method according to claim 52, wherein the coating material is copper or aluminium or a copper aluminium alloy.

54. A method according to any of claims 44 to 53, wherein the first layer is up to 150 micrometres in thickness.

55. A method according to any of claims 44 to 53, wherein the first layer is up to 100 micrometres in thickness.

56. A method according to any of claims 44 to 55, wherein the first layer is sprayed to at least 2 micrometers in thickness.

57. A method according to any of claims 44 to 56, wherein the layer of coating material is sprayed to cover the whole of the said surface of the substrate.

58. A method according to any of claims 44 to 57, the method comprising the step of: depositing the first layer of coating material at the surface of the substrate so that the first layer is incorporated in the organic material of the substrate.

59. A method according to any of claims 44 to 58, wherein after the step of depositing the first layer there is a step of removing any organic material on the first layer of coating material.

60. A method according to any of claims 44 to 59, wherein the first layer comprises a foil.

61. A method according to any of claims 44 to 59, wherein the first layer comprises powder particles.

62. A method according to claims 44 to 61, wherein the further layer is deposited by thermal spraying.

63. A method according to claim 62, wherein the further layer is deposited by plasma spraying.

64. A method according to any of claims 44 to 63, wherein the further layer is wholly or principally made of ceramic or metal or ceramic and metal.

65. A method according to any of claims 44 to 64, wherein the further layer is wholly or principally made of ceramic.

66. A method according to claim 64, wherein the further layer comprises at least 50 wt-% of at least one of zirconia, titania, and alumina.

67. A method as claimed in claim 66, wherein the further layer comprises wholly or principally at least one of zirconia, titania, and alumina.

68. A method as claimed in claim 66 or 67, wherein the further layer also includes at least one of yttria and magnesia.

69. A method according to any of claims 44 to 68, wherein the method includes depositing at least one additional layer on the further layer.

70. A method according to claim 69, wherein the or each additional layer is deposited by thermal spraying.

71. A method according to claim 70, wherein the or each additional layer is deposited by plasma spraying.

72. A method according to claim 69, claim 70, or claim 71, wherein the or each additional layer is made of ceramic or metal or ceramic and metal.

73. A method according to any of claims 44 to 72, wherein the further layer is deposited to be at least as thick as the first layer.

74. A method according to any of claims 44 to 72, wherein the further layer is deposited to be thicker than the first layer.

75. A method according to any of claims 44 to 74, wherein the further layer is deposited to be at least 100 micrometres thick.

76. A method according to any of claims 44 to 74, wherein the further layer is deposited to be at least 150 micrometres thick.

77. A method according to any of claims 44 to 76, wherein the further layer is deposited to be not greater than 300 micrometres thick.

78. A method according to any of claims 44 to 76, wherein the further layer is deposited to be not greater than 250 micrometres thick.

79. A method according to any of claims 44 to 78, wherein the substrate is a bicycle wheel and the layers are deposited on the area of the rim of the wheel which is frictionally clamped by brake blocks to brake the wheel.

80. A method according to claim 79, the bicycle wheel including a rim for a bicycle tyre, the rim including an outer surface wholly or principally of carbon fibre composite material, the method comprising depositing on the outer surface of the rim a first layer of coating material and a further layer, the further layer being wholly or principally of ceramic or metal or ceramic and metal and forming a braking surface to be contacted by a brake block.

81. A method according to claim 80, wherein the further layer is a layer wholly or principally of ceramic.

82. A method according to claim 81, wherein the further layer is at least 50% titanium dioxide.

83. A method according to any of claims 80 to 82, wherein the bicycle wheel is wholly or principally of carbon fibre composite material.

84. A method according to any of claims 44 to 78, wherein the substrate is the head of a golf club and the layers are deposited on at least one of the striking face and the ground engaging face of the golf club head.

85. A method as claimed in claim 84, the head of the golf club being wholly or principally of carbon fibre composite material, the method comprising depositing on at least one of the striking face and the ground engaging face of the golf club the first layer of coating material and a further layer, the further layer being wholly or principally molybdenum or tungsten.

86. A method according to any of claims 44 to 78, wherein the substrate is a medical implant.

87. A method according to claim 86, wherein the substrate is a bone or tooth implant.

88. A method according to claim 86 or claim 87, wherein the first layer is wholly or principally of silver.

89. A method according to claim 86, 87 or 88, wherein the further layer is wholly or

principally of titanium.

90. A method according to any of claims 86 to 89, wherein there is an additional layer wholly or principally of hydroxyapatite.

91. A method according to any of claims 44 to 90, wherein the coating material is sprayed at a rate of 100 g/min or less.

92. A method according to claim 91, wherein the coating material is sprayed at a rate of 70 g/min or less.

93. A method according to claim 92, wherein the coating material is sprayed at a rate of 40 g/min or less.

94. A method according to any of claims 44 to 93, wherein the further layer is sprayed at a rate of 150 g/min or less.

95. A method according to claim 94, wherein the further layer is sprayed at a rate of 100 g/min or less.

96. A method according to claim 95, wherein the further layer is sprayed at a rate of 50 g/min or less.