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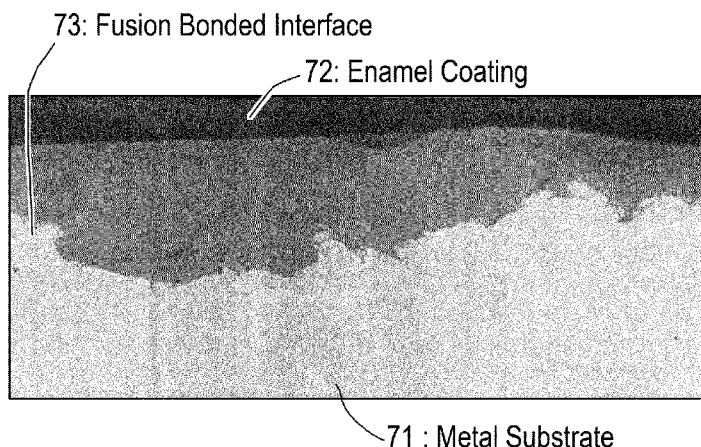
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Fig.7



(57) Abstract: A metal substrate (71) is coated with an enamel or other coating material (72) by irradiating the coating material (72) and substrate (71) with electromagnetic radiation to melt an underlying surface of the metal substrate (71) before melting the coating material (72) to create, after cooling, a fusion bond between the solidified substrate and coating material, whereby the fusion bonded interface (73) has an intermeshing irregular tongue and groove like microstructure profile shown in Figure 7. The electromagnetic radiation may be unfocussed, circilinear or focussed at a point located within the metal substrate (71) to first melt the substrate (71).



WO 2015/197811 A1

COATING METHOD AND COATED SUBSTRATE

The present invention relates to coated substrate and a method for coating a substrate, such as a pipe. The coating may protect the surface of the pipe or other substrate against corrosion and wear. The coated pipe or other substrate of the invention is applicable in oilfield applications.

Wellbores for the exploration and production of oil, gas or other minerals from subterranean reservoir layers are typically provided with protective casing or liner. These may include a pipe string lowered into an openhole section of the wellbore and cemented in place. Herein, the term casing is typically used to indicate a pipe string extending from surface into the wellbore, whereas liner may typically be used to indicate a pipe string which extends from a downhole location further down the wellbore. Hereinafter, the terms tubular or pipe will be primarily used, which may be equally applicable to casing and liner.

The casing or liner may be designed to withstand a variety of forces, such as collapse, burst, and tensile failure, as well as chemically aggressive brines. The casing string is typically assembled from multiple interconnected pipe sections, having a length of for instance about 10 metres each. Casing connections connect adjacent pipe sections. The casing sections may be fabricated with male threads on each end, wherein shorter-length casing couplings with female threads are used to join the individual sections of casing together. Alternatively, pipe sections may be fabricated with male threads on one end and female threads on the other. The pipe sections may be generally referred to as Oil Country

Tubular Goods (OCTG). Casing may be run to protect fresh water formations, isolate a zone of lost returns or isolate formation layers with significantly different pressure gradients. The operation during which the casing is put into the wellbore may be referred to as "running pipe."

Inside the innermost casing, a wellbore may typically be provided with another tubing string, typically referred to as production string or production tubing.

Herein, the production tubing may be assembled with other completion components to make up the production string. The production string is the primary conduit through which reservoir fluids are produced to surface. The production string is typically assembled with tubing and completion components in a configuration that suits the wellbore conditions and the production method. The tubing itself may be made up from interconnected pipe sections, in a similar fashion to the casing strings. An important function of the production string is to protect the primary wellbore tubulars, including the casing and liner, from corrosion or erosion by the reservoir fluid.

Interior surfaces of the production tubing and their associated connections are frequently subjected to one or more of relatively high temperatures, high pressures and highly corrosive fluids. Temperatures may range up to 350 degree F (175 degree C) or more. Pressures may be as high as 20,000 PSI (1400 bars) or more. The reservoir fluids may be highly corrosive, for instance due to the combination of hydrocarbons, CO₂ and/or H₂S in the presence of water. The use of secondary and tertiary enhanced recovery methods in hydrocarbon production, such as gas injection, water flooding and chemical flooding,

may further aggravate corrosive attack on the tubing in the wellbore.

Pipe sections for wellbore tubulars, including the casing or production tubular, are usually manufactured from steel of varying composition, which may also have been heat-treated to achieve the appropriate strength. The steel herein may include carbon steel or alloy steel. A wide variety of API grades are available, each indicating steel compositions and pipe strength for particular applications.

Alternatively, pipe sections may be specially fabricated of stainless steel, aluminum, titanium, fiberglass and other materials.

When produced from steel, these components are subject to attack by corrosion. Several types of corrosion mechanisms exist, including: erosion-corrosion (also known as impingement), stress corrosion cracking, sulphide stress cracking, pitting, and galvanic corrosion.

Corrosion in metals may be caused by the flow of electricity from one metal to another metal or from one part of the surface of one piece of metal to another part of the same metal where conditions permit the flow of electricity. Further, a moist conductor or electrolyte may be present for this flow of energy to take place. Energy passes from a negative region to a positive region via the electrolyte media.

Electrical contact or coupling of dissimilar metals frequently causes increased corrosion. This form of corrosion is generally referred to as galvanic corrosion. Galvanic corrosion is quite prevalent and troublesome, occurring in a wide variety of circumstances. For example, coupling aluminum and iron pipe together will

result in very rapid corrosion of the aluminum pipe section. The galvanic corrosion mechanism may be illustrated by considering the effect of electrically connecting zinc to platinum immersed in sea water. Under
5 these conditions, the platinum is inert and does not corrode, while the zinc is attacked. The reactions occurring on the surface of the zinc are the anodic oxidation of zinc to zinc ions, and the cathodic reduction of dissolved oxygen to hydroxide ions. If the
10 electrical potentials of these two metals are measured, the platinum would be found to have a positive potential, while the zinc would be found to have a negative potential. As may be appreciated, as the potential difference increases, galvanic corrosion increases.

15 Obviously, from a corrosion standpoint, the replacement of steel tubulars and associated hardware with materials less subject to corrosion would be highly desirable in gas and oil applications, if it were practical or economically viable. Non-metallic
20 components, such as fiberglass casing, tubing, sucker rods and the like are finding their way into oil field applications. Performance limitations, including service loads, pressures and temperatures, restrict the across-the-board replacement of metallic hardware, however. On
25 the other hand, pipe sections made of solid corrosion resistant alloy (CRA), such as stainless steel and nickel alloy, may provide sufficient corrosion resistance. But tubular sections made of solid corrosion resistant alloys are typically much more expensive than carbon steel. The
30 latter may render projects uneconomical. In addition, newly developed hydrocarbon reservoirs are producing increasingly corrosive hydrocarbons, for instance including a greater percentage of H₂S, requiring higher

grade Corrosion Resistant Alloys (CRAs). And higher grade CRAs are increasingly more expensive. For instance, compared to API grade P110 carbon steel, the same pipe section made of CRA may be up to 5, 10 or even 25 times
5 more expensive (when made of 316L, SM25CRW-110/125, or C22 CRA respectively).

Several manufacturing methods have been developed for producing corrosion resistant clad or lined carbon steel tubular, for instance for transporting oil and gas, to
10 achieve economic advantages over solid corrosion resistant alloy (CRA) tubular such as stainless steel and nickel alloy.

In various oil and gas applications, steel pipe is provided with a lining of corrosion-resistant material.
15 For example, it is known to bond various epoxy-based coatings to the interior of the pipe, as well as coatings containing polyethylene, polyvinyl chloride and other thermoplastic and thermosetting materials.

Of the various polymeric coating materials, arylene sulfide polymers have gained wide acceptance, see for
20 instance US-3354129. Generally, these polymers consist of a recurring aromatic structure coupled in repeating units through a sulfur atom. Commercially available arylene sulfide polymers which have been used for coating oil and
25 gas pipes and pipe couplings are polyphenylene sulfides. The polyphenylene sulfides used in oil and gas applications exhibit high melting points, outstanding chemical resistance, thermal stability and are non-flammable. They are also characterized by high stiffness
30 and good retention of mechanical properties at elevated temperatures as well as the ability to deform smoothly, thereby, for example, preventing the galling of threads, even at high thicknesses.

US-3744530 describes polyphenylene sulfide coated pipes, wherein the polyphenylene sulfide coating also contains a filler, such as iron oxide, in an amount of between 5% to 30%.

5 While polymeric coated pipes and couplings have gained wide acceptance in applications requiring corrosion protection, the cracking of such coatings during installation and in use tends to limit their insulating effect, increasing the likelihood that
10 galvanic corrosion will take place. This is particularly relevant in the female part or pin-end of the connections, where cracking may occur during assembly of the connection. Moreover, the polymeric coatings of threaded couplings are particularly prone to cracking due
15 to the stresses imparted during assembly of connections.

 JP-60 109686-A (KAWASAKI HEAVY IND LTD) 15 June 1985 (1985-06-15) provides a pipe system for transport of corrosive fluids. The pipe system comprises a tubular member made of a corrosion prone metal. Each tubular
20 member is provided with an inner lining of a corrosion resistant material. At each end, the tubular member and the inner lining are connected to a threaded coupling member, which is made of a corrosion resistant material. The tubular member and the liner are connected to the
25 threaded coupling member by a weld seam. But the cost saving from using clad steel rather than solid CRA is particularly valid when the total wall thickness of the pipe section increases. However, when the product of outer diameter (OD) times wall thickness (T) decreases,
30 the cost benefit of corrosion resistant alloy clad pipe versus solid CRA pipe decreases rapidly. For instance for pipe clad with Incoloy 825, the cost benefit with respect to solid CRA pipe is reduced to nil for tubulars having

smaller OD x T, such as typically used for production tubing.

While the use of corrosion resistant alloys for corrosion control has demonstrated superior corrosion resistance properties, they are quite costly and exhibit complex manufacturing and handling constraints. The price of high-performance steel for instance, which may include high percentages of nickel (for instance more than 8%), chromium (e.g. more than 18%) and/or molybdenum, may exceed the price of carbon steel with a factor of about 20 to 50. High-performance stainless steel however is often the material of choice in environments containing relatively large volumes of H₂S, for instance when the H₂S partial pressure exceeds 10 bars.

In oilfield applications, polymeric coatings will be unsuitable when the partial pressures of either CO₂, H₂S and/or water exceed a certain threshold, as these materials may permeate through the polymeric coating, which may lead to corrosion of the carbon steel base material.

US-5426278 discloses a laser irradiating torch device used to apply corrosion resistant coating or other coatings to an inner surface of small diameter piping. A laser beam generated outside the torch device is transmitted to the torch head in an optical fiber disposed longitudinally through the central axis of the piping. The focal point of the laser beam can be adjusted with a lens system whose location can be adjusted in the axial direction. The transmitted laser beam is reflected radially out of the torch device with a reflection mirror, and the lens system is adjusted so that the laser beam is focused near the inner surface of the piping. When the torch device is inserted in the

15 piping, a centering device aligns the torch body and the torch head centrally within the piping so that the revolving axis of the torch device coincides with the central axis of the piping. When the torch head is rotated and the laser beam turned on, the inner wall surfaces of the piping is heated uniformly to produce a coating.

10 The coating method of US-5426278 provides a coating having superior corrosion resistant properties. Still, the CRA material of the coating renders the small diameter pipe relatively expensive, as explained above.

Other known coating techniques are disclosed in US patent application US2013/087952 and European patent application EP0221276.

15 International patent application WO98/54379 discloses the method according to the preamble of claim 1. The known method involves coating of a sintered metallic body with a laser-deposited cermet coating using a laser beam that melts the coating material and underlying surface of the sintered body to create a metallurgical bond therebetween and to completely fuse the cermet coating powders. A disadvantage of this known method is that there is no sequence in which the coating material and underlying metallic surface are molted, which may generate a poor metallurgical bond.

The invention aims to provide an improved method and coated pipe or other substrate which overcomes at least some of the drawbacks of the prior art.

30 The invention provides a method for coating a metal substrate, the method comprising the steps of:

- depositing a coating material on an underlying surface of the metal substrate, the coating material

having a coating melting temperature which exceeds the substrate melting temperature;

- irradiating the metal substrate and coating material with electromagnetic radiation to melt the coating material and the underlying surface of the metal substrate; and

- cooling the metal substrate and coating material to create a solidified coated metal substrate;

- characterized in that the underlying surface of the metal substrate is molten before melting the coating material to generate a fusion bond between the solidified metal substrate and coating material.

Focusing the electromagnetic radiation below the interface, i.e. below the surface of the substrate rather than the surface of the coating, creates a larger, lower intensity heated zone, in combination with using a coating material that has a melting temperature which is higher than steel. The larger area creates time for the heat to conduct to the under-lying steel, which, because it has a lower melting temperature, can melt first. As the temperature rises further the enamel or other coating now also melts on top of the molten steel. This is better than melting the enamel or other coating directly with a focused laser, which leads to much more turbulence/distortion in the enamel or other coating material.

In order to effectively melt the enamel or other coating material without affecting the microstructure of the underlying base metal, suitably the heating is provided in the form of radiant energy.

In an embodiment, the laser is completely defocused. Thus, bonding of the coating material and the metal is achieved without deep penetration of heat into the base

metal and without undesired microstructure changes of the base metal. The process of laser treatment may provide a fully melted or a sintered enamel coating. In the latter case the coating may have some residual porosity which can be an additional source of ductility, thereby improving the resistance of the coating to bending stress and impact in general.

The laser beam may comprise a linear laser beam, which may direct light to the substrate in the form of a point located within the substrate. In such application, the point of light provided by the laser beam can be moved relative to the surface to irradiate the entire surface. Such movement can be achieved by rotating the pipe around a laser beam apparatus, or by rotating the laser beam.

In an embodiment, the linear laser beam is converted into a circilinear laser beam. The latter may provide an annular ring of light, to light the inner surface of a pipe along its circumference. The entire inner surface can be irradiated by moving the ring in axial direction through the pipe, to achieve a uniform distribution of the radiant energy along the inner surface. A circilinear laser beam herein implies a laser beam that provides not only a dot of light but rather an annular line on the inner surface. Patent application WO-2012/032116-A1 discloses an example of an apparatus for generating a circilinear laser beam. Herein, the laser beam can have a circular cross-sectional shape whereby the laser beam radiates along a circular line on the contact surface. Thus, rotation of the inner surface of the pipe and the laser beam is obviated, and only axial movement is required, providing a smoother, more even coating.

The combination of laser de-focusing and high melting temperature enamel reduces disturbance, turbulence, and mixing in the melted zone, leading to a smoother and less mixed end result. By embedding the enamel coating in the metal substrate due to partial melting of both the coating and a top layer of the metal, the enamel is embedded in the metal substrate, thus preventing premature failure of the enamel coating and in general making the coating more resilient to withstand bending stress and other types of impact. Thus, the method of the invention allows to coat the inner surface of a pipe with a relatively cheap enamel coating, enabling said inner surface to withstand the corrosion prone environment in a wellbore.

According to another aspect, the invention provides a coated substrate, comprising:

- a metal substrate having a surface;
- a layer of molten coating material provided on said surface; and
- an interface layer interposed between the surface and the layer of molten coating material, the interface layer comprising a mixture of molten coating material and molten metal coating material and molten metal entangled in a fusion bond.

In a preferred embodiment, the metal substrate is a pipe section, the surface is an inner surface of the pipe section, and the coating material comprises enamel, providing a pipe section having an enamelled inner surface.

By melting or sintering the enamel coating on the underlying metallic surface, followed by solidification of the molten metal and coating, an interface layer is created wherein the metal of the substrate and the

material of the coating are mixed, improving a fusion between the coating and the base metal, wherein the fusion bonded interface has an irregular tongue and groove like microstructure substantially as illustrated in Fig.7. In view thereof, the coating is able to withstand higher contact and bending stresses. Furthermore, the molten coating spreads along the surface of the metal substrate, so that after solidification of the metal, the coating has a smooth surface.

The invention will be described in more detail and by way of example with reference to the accompanying schematic drawings in which:

Fig. 1 shows a cross-section of an embodiment of a method to apply a coating material to an inner surface of a pipe;

Fig. 2 shows a cross-section of a metal substrate provided with the coating material, irradiated and heated according to a method of the invention;

Fig. 3 shows a cross-section of the metal substrate provided with the coating material, while being irradiated according to a method of the invention;

Fig. 4 shows a diagram indicating hardness of the metal substrate on the y-axis after irradiation according to the invention versus distance from the surface of the metal substrate on the x-axis;

Fig. 5 shows a detail of a cross-section of an embodiment of a metal substrate provided with a coating according to the invention;

Fig.6 is diagram that shows a material distribution(k) at a fusion bonded interface between a metal substrate and enamel coating made with the sequential heating method according to the invention; and

Fig.7 is a longitudinal sectional view of a fusion

bonded interface between an enamel coating and a metal substrate made with the sequential heating method according to the invention.

5 In the figures and the description, like reference signs relate to like components.

Fig. 1 shows a longitudinal cross-section of a tubular pipe 1. A central longitudinal axis of the pipe is indicated by line 2. The pipe has inner surface 4 and outer surface 6. The pipe may be a tubular section
10 selected from typical Oil Country Tubular Goods (OCTG), including casing or liner for a wellbore. Opposite ends 8, 10 of the pipe section 1 may be provided with threaded connectors to connect the pipe section to another pipe section. The connectors (not shown) typically comprise a
15 pin member and a box member interconnectable with the pin member.

Initially, a selected surface, for instance inner surface 4, may be cleaned. Subsequently, a layer of coating material is applied to the selected surface. For
20 example, the coating material may be applied by thermal spraying, electroplating, or brushing.

A coating device 20, for instance a torch 22, may be axially moveable with respect to the pipe 1. The coating device can deposit a layer 24 of coating material 26 on
25 a selected surface of the pipe, such as the inner surface 4. The coating material may comprise enamel.

The enamel coating material may comprise one or more of weight fractions: SiO₂ (e.g. 1 to 50%), B₂O₃ (e.g. 0 to 20%), Na₂O (e.g. 4 to 20%), Al₂O₃ (e.g. 0.5 to 15%),
30 K₂O (e.g. 0.2 to 8%), CaO (e.g. 0.1 to 3%), CaF₂ (e.g. 0 to 15%), ZrO₂ (e.g. 0-16%), MnO₂ (e.g. 0 to 4%), NiO (e.g. 0 to 2%), CoO (e.g. 0 to 2%), Cu₂O₃ (e.g. 0 to 8%),

Zn₂O₃ (e.g. 0 to 4%), Cr₂O₃ (e.g. 0 to 4%), Fe₂O₃ (e.g. 1 to 40%).

The enamel coating material may be a mixture of silica (silicium oxide) and alumina (aluminium oxide).

5 Conventional vitreous enamel is glass bonded by fusion to a metal surface. The most common glass is a fusion of silica, soda, lime, and a small amount of borax. Though normally transparent, various amounts of opacity can be produced by adding or growing crystals
10 within the glass structure. A wide range of colors are produced by incorporating certain elements, mostly transition metals. The physical properties of the glass can be controlled to permit bonding to most metals, including steel, aluminum and titanium. The word "Enamel"
15 refers to the glass material, as well as to the finished product.

 The enamel (glass) coating material is crushed to a powder. The powder may be somewhat finer than granulated sugar and somewhat coarser than flour. The powder is
20 applied, by one of several methods, to the selected metal surface.

 As shown in Fig. 1, an embodiment to deposited the powdered enamel coating material on the inner surface 4 of the pipe 1 may be an axially moveable torch 22. An
25 example of a suitable torch system for depositing the powdered enamel coating 26 is, for instance, provided in US-5426278 or EP-1247878.

 Conventionally, the metal article provided with the powder coating is heated to 1000 to 1600 °F (530 to 870
30 °C), either in a preheated furnace or with a torch. After 1.5 to 10 minutes, the article is removed and allowed to cool to room temperature. Subsequent coats can be

applied. For instance, 10 to 20 layers of coating can be applied consecutively to bring about the desired results.

However, the steel of OCTG pipes typically has a particular API grade, indicating a particular steel composition and strength suitable for a particular application. For instance:

i) P110 grade alloy steel, typically for deep water applications. Yield Strength may be between 758 MPa min and 965 MPa max (110,000 psi min and 140,000 psi max);

ii) L80 is usually used in wells with sour (hydrogen sulfide) environments. Yield Strength may be between 552 MPa min and 655 MPa max (80,000 psi min and 95,000 psi max). Hardness may be between 23 Max HRC and 241 Max HBW;

iii) T95 is an API controlled yield strength grade, generally for use in sour condensate wells. Yield Strength is between 655 MPa min 758 MPa max (95,000 psi min and 110,000 psi max). Hardness is between 25 Max HRC and 255 Max HBW; and

iv) Q125 is an API grade for deep well service, not generally for use in sour condensate wells. Yield Strength may be between 862 MPa min and 1,034 MPa max (125,000 psi min and 150,000 psi max).

Heating the steel of the pipes as referenced above in a furnace or with a torch to apply an enamel coating will negatively affect one or more of the particular qualities of the steel, most notably yield strength and hardness. This would render the pipe unsuitable for application in a wellbore, as this may greatly increase the chance of well control incidents due to failed casing. Also, conventional enamel coating is particularly brittle, meaning that for instance chips of the enamel coating may readily come off, even upon relatively minor impact.

As indicated in Fig. 2, in a method of the invention, the coating layer 24 is irradiated with electromagnetic radiation 40. The radiation may be focused, using lens system 42 or similar optical focusing means. The focused radiation 44 is focused below the surface 4 of the metal substrate 1. I.e., focus 46 of the focused radiation 44 is located at or below the surface of the metal substrate 1, rather than in or above the coating 24. Herein, the width 48 of the radiation beam when it arrives at the surface of the coating 24 is wider than the width of the focused beam at point of focus 46. The wider beam at the surface means that the energy of the radiation is spread over a larger area leading to slower and more even heating of the coating 24 and the metal 1.

Defocusing of the radiation 40 herein may be in the range starting from slight defocusing, wherein the focus 46 is located at or just below the surface 4, to complete defocusing wherein the width 48 is equal to original width 50 of the radiation 40 as it arrives at the optical system 42. The latter may be achieved by removing the optical system 42 altogether, or by moving the optical system 42 in close proximity to surface 52 of the coating layer 24.

To create a coating according to the invention, the applied coating layer 24 is irradiated at a selected location as described above with respect to Fig. 2, until heat dissipated in the coating 24 and the metal substrate starts to melt a top section 54 of the metal substrate near the surface 4 thereof, and subsequently also melts the coating layer 24 providing a locally melted coating 56. As indicated in Fig. 3, the surface 52 of the coating layer 24 starts to glow when the coating has locally

melted. The glowing section 58 of the coating indicates that the coating has melted sufficiently. The glowing section can, for instance, be monitored by visual inspection.

5 Once the glowing section 58 indicates sufficient melting of the coating and the top 54 of the metal substrate, the beam 44 of electromagnetic radiation is moved along the metal substrate in the direction of arrow 59. Moving the beam 44 continues until the coating layer 10 24 has been melted along a preselected length of the metal substrate 1.

 When the beam 44 has passed, the molten coating material and the molten top section of the substrate 1 are allowed to cool. The cooled coating material creates 15 an interface layer 60 at the surface of the metal substrate and a coating layer 62 on the interface layer. The coating layer comprises cooled and hardened coating material. The interface layer 62 comprises a mixture of the metal of the metal substrate and the coating 20 material, providing good bonding of the coating to the substrate.

 The linear laser beam 36 induces a laser line as opposed to the more general laser point, and has sufficient energy to induce melting of the galling 25 resistant metal on the contact surface 22.

 The coating layer 24 may have a thickness between 10 μm and 1 mm, preferably between about 200 and 300 μm .

 In a preferred embodiment, the radiation 40 is laser light, for instance in the visible spectrum. The 30 radiation energy of the laser beam is sufficient to cause melting of the coating and the top of the metal substrate. The molten coating material and the molten metal flow, to form a uniform coating layer 62. Since the

molten coating can flow, the coating layer 62 has a uniform thickness and a smooth outer surface.

In a practical embodiment, thickness of the coating layer is in the order of 20 μm to 2 mm. Thickness of the coating is preferably in the order of 100 to 300 μm .

The present invention may also provide a method for coating an inner surface of a pipe, in particular an OCTG (Oil Country Tubular Goods) pipe, with a coating. Coating the inner surface of the pipe allows the use of relatively cheap pipe, made from relatively low-cost steel, which is subsequently provided with a suitable coating layer in accordance with the method of the invention, to provide corrosion resistance.

Laser melting of the applied coating layer may be challenging when the entire inner surface of an OCTG pipe section has to be treated. Herein, one pipe section typically has a length in the order of 10 meters. The entire inside surface of the pipe section may be irradiated by laser, for instance using a method or system as described in WO-2013/117754. Other suitable laser systems are for instance described in WO-2012/156230, WO-2012/95422, WO-2012/32116, and WO-2012/76651. Any combination of these laser systems may also be used.

Heating the coating on the metal will, as described with reference to Fig. 3, create an interface layer which will be affected by heating. The remainder of the metal substrate however will not be negatively affected.

As shown in Fig. 4, a heat-affected zone (HAZ) of the metal substrate can extend from the surface 4 of the metal to thickness T1. Herein, properties of the metal are most affected near the surface 4 of the metal, and gradually improve to the standard properties in the remainder of the

metal. As an example, shown in Fig. 4, the heat affected zone may extend along up to T1 being about 0.5 to 1.5 mm.

For OCTG pipe, total wall thickness of the pipe may be significant. Production casing or production tubing, i.e. the innermost pipe strings in a wellbore which have to withstand reservoir pressures and are most exposed to corrosive wellbore fluids, typically have a wall thickness T in the range of 0.5 inch (1.2 cm) to T exceeding 1 inch (2.4 cm). The HAZ then may cover $T_1 / T = 1.5 / 12$ is about 12.5% of the total T. A lower limit is provided by $0.5 / 24$ is about 2%. Typically, the wall thickness T is greater than 0.5 inch, indicating that the HAZ generally can be limited to affecting about 10 to 2% of the wall thickness, or less. Thus, the extent of the HAZ can be limited to an acceptable limit with respect to the total wall thickness of the pipe, wherein properties of the pipe remain within acceptable levels.

The exemplary diagram shown in Fig. 4 indicates hardness expressed in units HK on the y-axis. The example indicates that the hardness reduction in the heat affected zone may be limited to $250 / 350$ is about 0.7 at the surface 4 of the pipe. Hardness reduction a between the surface 4 and T1 is more modest, in the range of about 20% to 5% or less.

Fig.6 is a diagram showing a material distribution(k) at a fusion bonded interface between a metal substrate and enamel coating made with the sequential heating method according to the invention, wherein curves I-V show the weight distribution (k) of Chromium(I), Manganese(II), Aluminium(II), Silicon(IV) and Iron(V) at both sides of a fusion bonded interface (73), which is located in the middle of the horizontal axis near the 20 μ m mark and the distance from the fusion

bonded interface is measured in μm .

Fig.7 is a longitudinal sectional view of a fusion bonded interface 73 between an enamel coating 72 and a metal substrate 71 made with the sequential heating method according to the invention. The fusion bonded interface 73 is an irregularly shaped interface where the surfaces of the enamel coating 72 and metal substrate 71 are entangled and intermesh in an irregular tongue and groove like profile, which enhances the metallurgical fusion bond between the enamel coating 72 and metal substrate 71.

As indicated above, the method of the present invention allows coating of a metal substrate, including the inner surface of OCTG such as (production) casing and tubing, with a relatively cheap material. The method provides good bonding to the substrate, while the interface layer wherein the metal and the coating material are intimately mixed in a irregular tongue and groove like pattern, which allows ductility and bending of the coating to obviate chipping thereof.

The cost reduction provided by the coating of the present invention is indicated below, wherein the top row indicates the pipe material or additional coating material on the pipe, and the bottom row indicates a cost estimate in Euros:

Carbon steel 90 ksi	Inconel 625 solid pipe	Butting quote	Additional CRA Nano coating	Add. spray coating	Add. Enamel coating
400	10,000	6300 - 8150	3500 - 9000	2500 - 3500	180 - 250

Bendability of the coated metal surface may be indicated by the following examples, wherein the left column indicates respective samples and the right column indicates strain to break in percent (%), providing a measure of bendability:

Sample	Strain to break (%)
1 (B2L)	1.49
2	1.50
3	1.45
4 (A10)	1.39
5 (A8)	1.52
6 (A6)	1.42
7 (A1)	1.43
8 (G)	1.38
9 (L)	1.49
10 (K)	1.34

The present invention is not limited to the embodiments thereof as described above, wherein many modifications are conceivable within the scope of the appended claims. Features of respective embodiments may for instance be combined.

C L A I M S

1. A method for coating a metal substrate, the method comprising the steps of:

- 5 - depositing a coating material on an underlying surface of the metal substrate, the coating material having a coating melting temperature which exceeds the substrate melting temperature;
- irradiating the metal substrate and coating material with electromagnetic radiation to melt the coating material and the underlying surface of the metal substrate; and
- 10 - cooling the metal substrate and coating material to create a solidified coated metal substrate;
- 15 - characterized in that the underlying surface of the metal substrate is molten before melting the coating material to generate a fusion bond between the solidified metal substrate and coating material.

2. The method of claim 1, the step of irradiating the coating material comprising focussing the electromagnetic radiation to a point of focus located below the underlying surface of and within the metal substrate thereby melting the underlying surface of the metal substrate before melting the coating material and

25 creating and metal a fusion bonded interface with an irregular tongue and groove like microstructure between the solidified coating material and metal substrate.

3. The method of claim 1 or 2, wherein the coating material comprising enamel, the step of irradiating the substrate and coating material providing a fusion bonded enamelled metal substrate.

30

4. The method of claim 3, wherein the coating material comprises weight fractions comprising one or more of:

SiO₂ 1 to 50 weight%, B₂O₃ 0 to 20%, Na₂O 4 to 20%, Al₂O₃ 0.5 to 15%, K₂O 0.2 to 8%, CaO 0.1 to 3%, CaF₂ 0 to 15%, ZrO₂ 0-16%, MnO₂ 0 to 4%, NiO 0 to 2%, CoO 0 to 2%, Cu₂O 0 to 8%, ZnO 0 to 4%, Cr₂O₃ 0 to 4%, Fe₂O₃ 1 to 40%.

5 5. The method of claim 3, wherein the enamel comprises a mixture of silica and alumina.

6. The method of any of claims 1 to 5, wherein the electromagnetic radiation is visible laser light.

10 7. The method of claim 1 or 2, wherein the step of irradiating the coating material comprises substantially completely defocusing the electromagnetic radiation.

8. The method of any of the previous claims, the metal substrate forms part of a downhole well casing, liner, production tubing and/or surface tubular or vessel used in the hydrocarbon production and/or conversion industry.

15 9. The method of claim 8, the surface being an inner surface of the casing, liner and/or other tubular or vessel.

20 10. The method of claim 9, the step of irradiating the coating material comprising the steps of:

providing optical projection means for transforming a linear laser beam into a circilinear laser beam; and

25 moving the optical projection means in axial direction through the pipe section to irradiate the coating material on the inner surface of the pipe section with the circilinear laser beam.

30 11. The method of any of the previous claims, the step of depositing the coating material comprising depositing the coating material using thermal spraying, electroplating, brushing, and dipping.

12. A coated substrate made in accordance with the method of any one of claims 1-11, comprising:

- a metal substrate having a surface;

- a layer of molten coating material provided on said surface; and

- an interface layer interposed between the surface and the layer of molten coating material, the interface layer comprising coating material and molten metal entangled in a fusion bond.

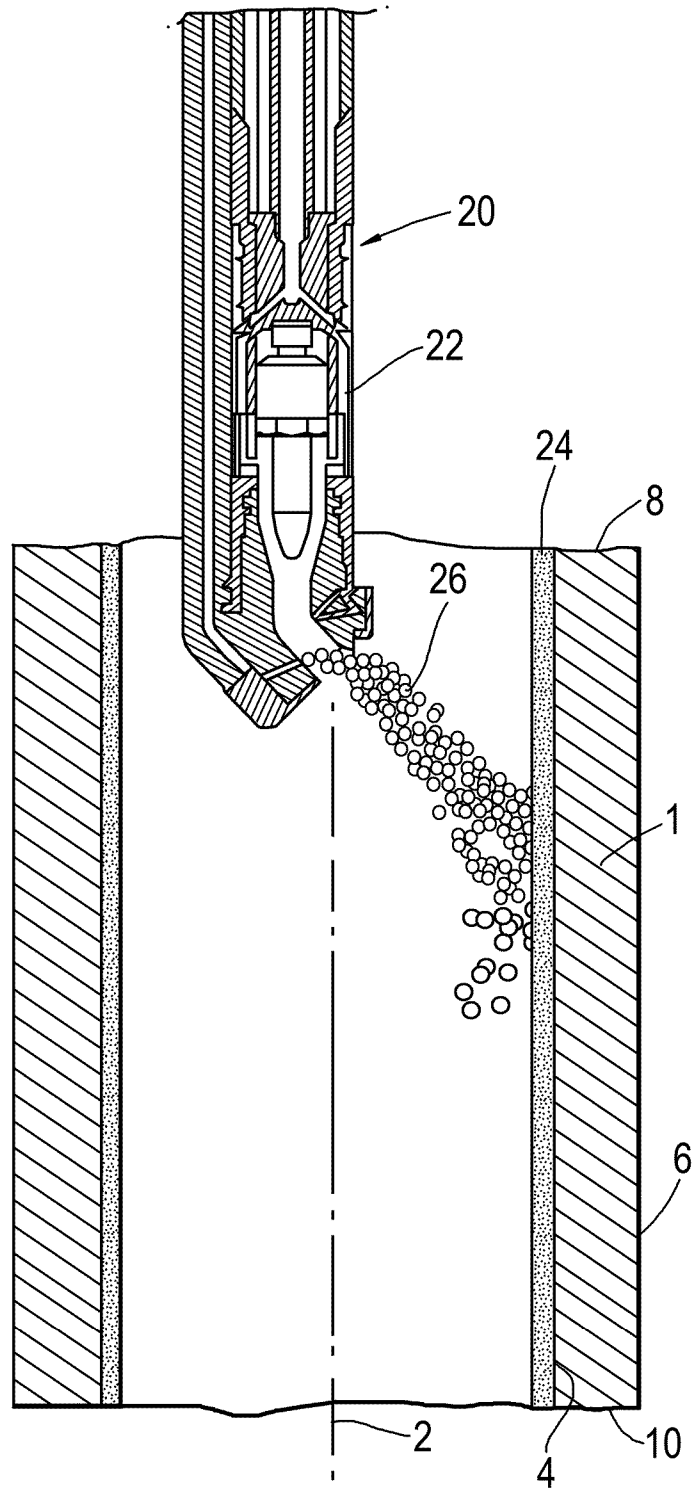
13. The coated substrate of claim 12, the metal substrate forming part of a downhole well casing, liner, production tubing and/or surface tubular or vessel used in the hydrocarbon production and/or conversion industry.

14. The coated substrate of claim 13, wherein the coating material comprises weight fractions comprising one or more of: SiO₂ 1 to 50 weight%, B₂O₃ 0 to 20 weight%, Na₂O 4 to 20 weight%, Al₂O₃ 0.5 to 15 weight%, K₂O 0.2 to 8 weight%, CaO 0.1 to 3 weight%, CaF₂ 0 to 15 weight%, ZrO₂ 0-16 weight%, MnO₂ 0 to 4 weight%, NiO 0 to 2 weight%, CoO 0 to 2 weight%, Cu₂O 0 to 8 weight%, ZnO 0 to 4 weight%, Cr₂O₃ 0 to 4 weight %, Fe₂O₃ 1 to 40 weight%.

15. The coated substrate of any one of claims 12-14, wherein the coated substrate comprises a fusion bonded interface with an irregular tongue and groove like microstructure between the solidified coating material and metal substrate substantially as illustrated in Fig.7.

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Fig.1



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Fig.2

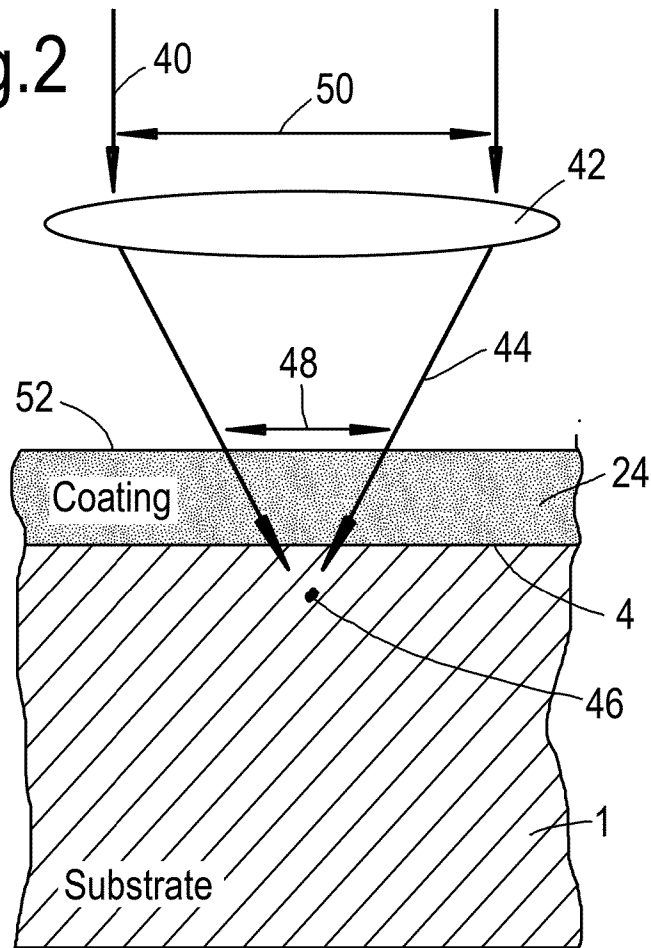
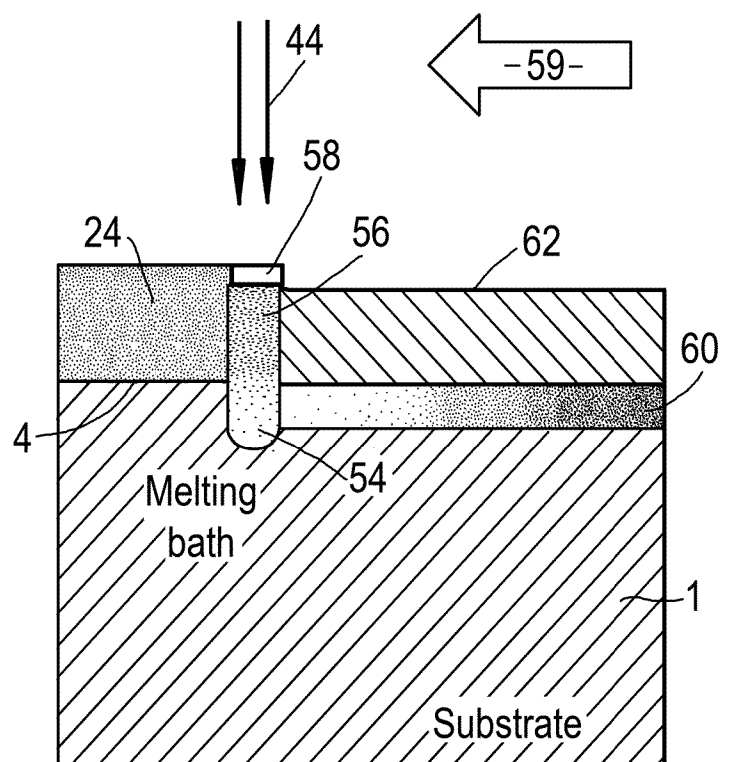


Fig.3



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Fig.4

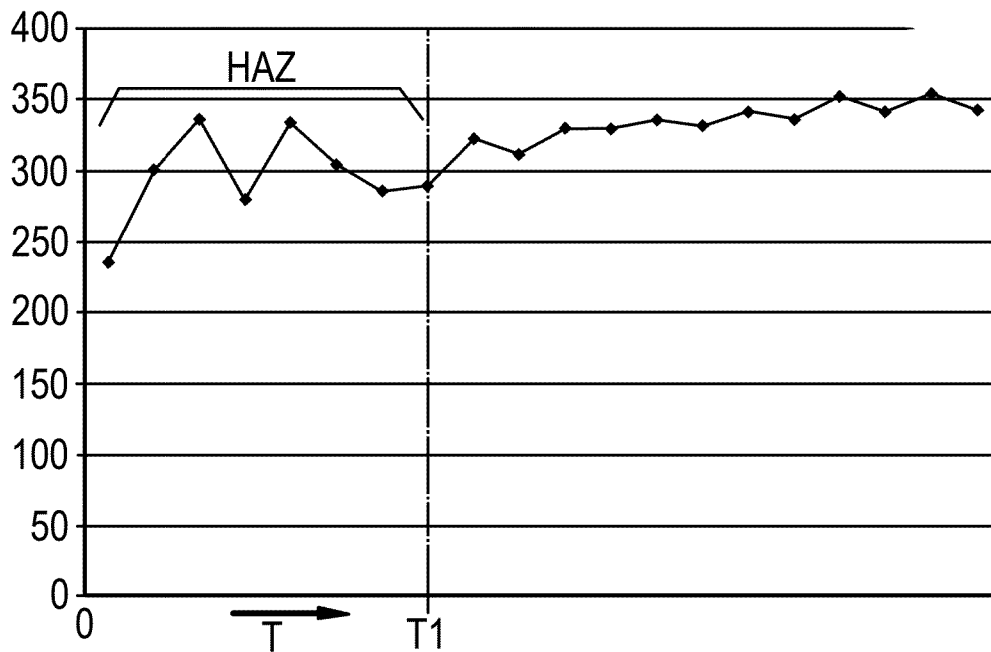
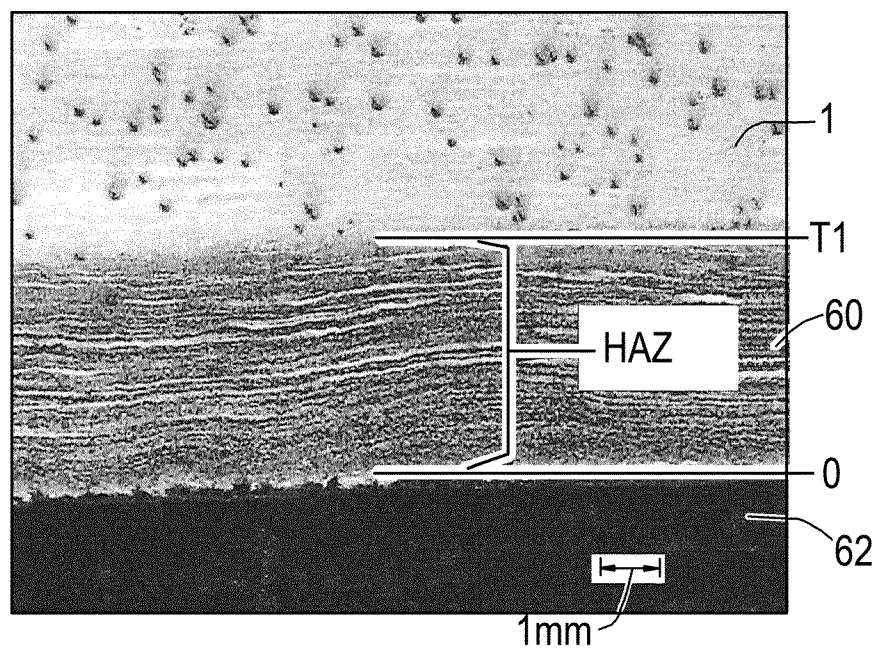


Fig.5



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Fig.6 Material Distribution (k)
at Fusion Bonded Interface

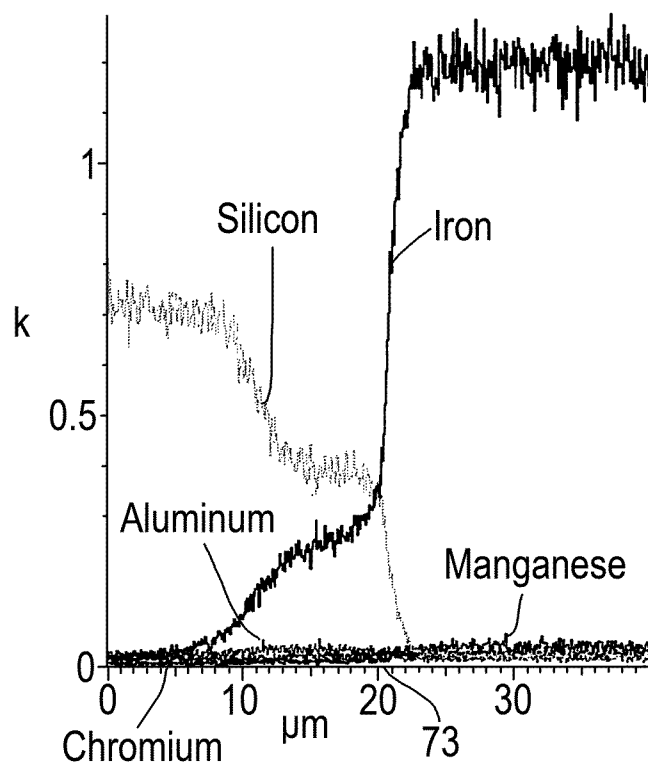
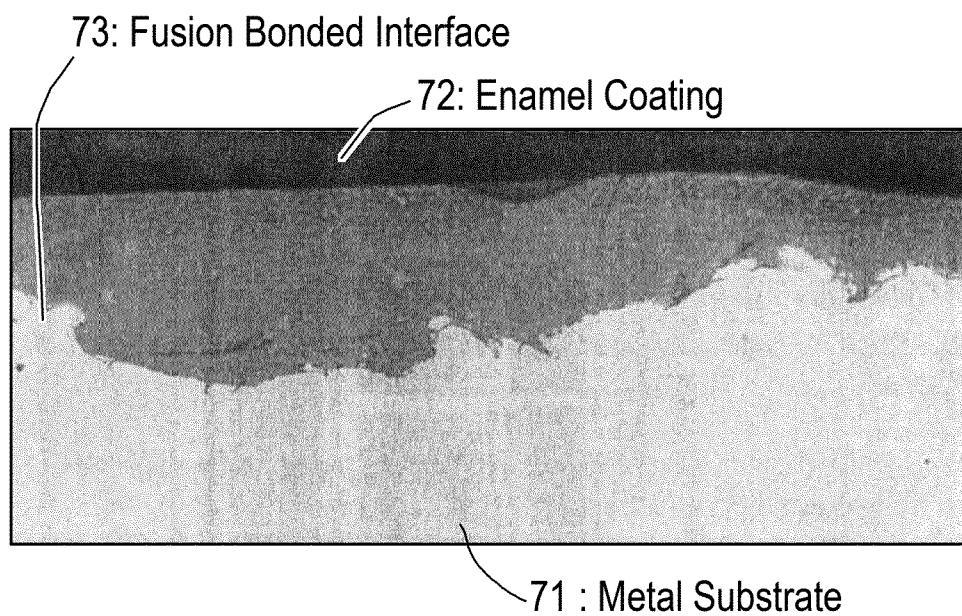


Fig.7



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/064496

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C24/00 C23C26/00 C23D1/00 C23D5/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C C23D

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98/54379 A1 (CARON PAUL [CA]) 3 December 1998 (1998-12-03) page 1, line 27 - line 29 page 3, line 2 - line 8 page 3, line 19 - line 20 page 6, line 17 - line 18 claim 12	1,12
A	US 2013/087952 A1 (WANG REN-BO [CN] ET AL) 11 April 2013 (2013-04-11) paragraphs [0011], [0013], [0014]; claim 1; figure 1 ----- -/-	1,12



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 August 2015

Date of mailing of the international search report

09/09/2015

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Fax: (+31-70) 340-3016

Authorized officer

Slembrouck, Igor

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/064496

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 221 276 A1 (TOYOTA MOTOR CO LTD [JP]) 13 May 1987 (1987-05-13) page 1, line 15 - line 20 page 2, line 22 - page 3, line 1 page 7, line 19 - page 8, line 5 page 21, line 11 - line 14 page 22, line 14 - page 23, line 8 page 28, line 22 - page 29, line 4 figures 3,13 -----	1,12
A	US 2009/093881 A1 (BANDYOPADHYAY AMIT [US] ET AL) 9 April 2009 (2009-04-09) paragraph [0068]; figure 5; example 1 -----	2
A	DE 10 2004 001722 A1 (MTU AERO ENGINES GMBH [DE]) 4 August 2005 (2005-08-04) paragraph [0025]; figures 3,4 -----	2
A	EP 0 264 779 A1 (COMP GENERALE ELECTRICITE [FR]) 27 April 1988 (1988-04-27) column 5, line 32 - line 46; claims; figures; examples -----	2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2015/064496

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1, 3-15(all partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1, 3-15(all partially)

Present claim 1 relates to a method which has a given desired effect, namely:

"characterized in that the underlying surface of the metal substrate is molten before melting the coating material".

This constitutes an attempt to define the subject-matter in terms of the result to be achieved, which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result.

The description does not provide support and disclosure in the sense of Article 6 and 5 PCT for any such method having the said effect and there is no common general knowledge of this kind available to the person skilled in the art. This non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of the claim (PCT Guidelines 9.19 and 9.20).

The search of claim 1 was consequently restricted to the specifically disclosed method having the desired effect, namely the scope of claim 1 was restricted according to the technical features of claim 2.

Any further reference to claim 1 should be understood as "claim 1 as searched" i.e. "claim 1 restricted by the technical features of claim 2".

The scope of any claim depending (directly or indirectly) from claim 1 (i.e. claims 3-15) is consequently restricted accordingly.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/064496

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