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(54) Title: SINGLE SIDED COATED METAL STRIP

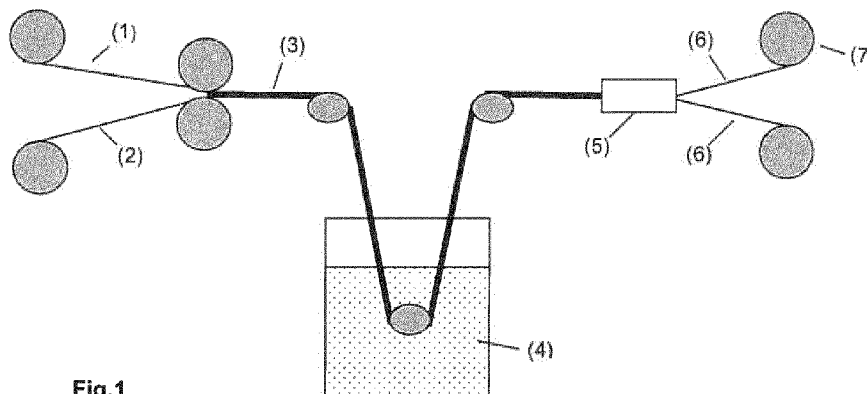


Fig. 1

(57) Abstract: The invention relates to a method for manufacturing a coated metal strip, which comprises the steps of: (i) providing a metal strip stack comprising a first metal strip and a second metal strip, the first metal strip having a first inner surface and a first outer surface and the second metal strip having a second inner surface and a second outer surface; (ii) providing a coating material on the metal strip stack, wherein at least the first outer surface and the second outer surface are coated with the coating material and wherein at least a portion of the first inner surface and the second inner surface are not coated with the coating material; (iii) separating the coated first metal strip and the coated second metal strip to provide two single sided coated metal strips.



## SINGLE SIDED COATED METAL STRIP

The invention relates to a method for manufacturing a single sided coated metal strip and to the single sided coated metal strip thus produced. The invention further  
5 relates to a laminate comprising the single sided coated metal strip.

Coatings are generally applied to improve the surface properties of a substrate. For instance, metallic coatings may be applied by galvanising to protect the substrate from corrosion. Galvanising is the process of applying a protective zinc or zinc alloy coating on a metal substrate such as iron, steel or aluminium. Methods for galvanising  
10 are known and include hot-dip galvanising, electrogalvanising and physical vapour deposition (PVD). Similarly, aluminium based coatings may be applied by hot-dip aluminising or by electroplating. Organic and/or inorganic coatings may also be applied to improve the appearance and/or adhesion properties of a substrate and/or to protect a previously applied metallic coating. Such coatings may be applied on both sides of a  
15 metal strip by roller coating or by spray coating. While the above techniques are suitable for providing coatings on both sides of a metal substrate, in certain applications it is desirable that only one surface of the metal substrate is coated. This is particularly true in the field of metal-polymer-metal laminates and for products that are to be used in building and construction applications where aesthetic appearance is  
20 of importance.

'Single sided' galvanised steel substrates can be produced by electrogalvanising. However, a small amount of zinc is always deposited on the other surface of the steel substrate and therefore the process may require a post-treatment to remove zinc from the 'uncoated' surface. A further disadvantage relates to the  
25 relatively expensive manufacturing route, which comprises the step of passing an electric current between an anode (zinc) and a cathode (steel substrate).

Hot-dip galvanising comprises the step of immersing a metal substrate in a bath of molten zinc or zinc alloy, such that each surface of the metal substrate is coated. However, methods for producing single sided galvanised steel by hot-dip galvanising are  
30 also known. According to US3177085 a colloidal silica coating is provided on one surface of a steel sheet or strip prior to immersing the coated sheet or strip in a hot-dip galvanising bath in order to prevent the zinc adhering to the coated surface. After galvanising, the colloidal silica coating is removed. Since an additional process step is required to remove the coating, the speed at which single sided galvanised steel  
35 substrates are manufactured is reduced. Moreover, at elevated temperatures the colloidal silica coating may delaminate exposing the 'uncoated' surface to the molten zinc. A method for producing single sided galvanised steel by hot-dip galvanising is also

known from US4120997, wherein a steel sheet or strip is differentially hot-dip coated to provide a metallic zinc coating on one surface of the strip and an ultra thin metallic zinc film on the other surface. The zinc film is then heated to form a zinc-iron intermetallic which is subsequently removed. Not only does this require an additional process step to  
5 remove the temporary coating, it also results in a substantial waste of zinc, which in recent years, has become increasingly expensive.

It is an object of the invention to provide an improved method for manufacturing single sided coated metal substrates.

Another object of the invention is to increase the volume and rate at which single  
10 sided coated metal substrates may be manufactured.

Further objects include providing a less expensive method for providing a single sided coated metal substrate and providing a single sided coated metal substrate that is suitable for use in metal-polymer-metal laminates.

One or more of the above objects are satisfied by the present invention, which  
15 according to a first aspect defines a method for manufacturing a coated metal strip which comprises the steps of:

- (i) providing a metal strip stack comprising a first metal strip and a second metal strip, the first metal strip having a first inner surface and a first outer surface and the second metal strip having a second inner surface and a second outer  
20 surface;
- (ii) providing a coating material on the metal strip stack, wherein at least the first outer surface and the second outer surface are coated with the coating material and wherein at least a portion of the first inner surface and the second inner surface is not coated with the coating material;
- (iii) separating the coated first metal strip and the coated second metal strip to  
25 provide two single sided coated metal strips.

By stacking the first metal strip and the second metal strip the first inner surface and the second inner surface are prevented from coming into contact with the coating material. Thus, pre-treatment of the first inner surface and the second inner surface, i.e.  
30 with a protective temporary coating, is not necessary. Moreover, the requirement to remove a temporary coating formed prior to or during the coating step is also avoided. Since the method of the invention does not require the application and/or removal of a protective temporary coating, the rate at which single sided coated metal strips are manufactured may be increased. The method of the invention also has the advantage  
35 that the number of single sided coated metal strips produced may be increased by a factor of two relative to conventional methods, since two metal strips are coated in the coating step instead of one.

In a preferred embodiment of the invention the coating material is a metal or metal alloy comprising zinc and wherein the zinc alloy comprises more than 50 % zinc and one or more of Mg, Al, Si, Mn, Cu, Fe and Cr. Zinc alloys selected from the group consisting of Zn-Mg, Zn-Mn, Zn-Fe, Zn-Al, Zn-Cu, Zn-Cr, Zn-Mg-Al and Zn-Mg-Al-Si  
5 are preferred and afford additional corrosion protection to the underlying metal strip by sacrificial protection.

In a preferred embodiment of the coating material is a metal or metal alloy comprising aluminium and wherein the aluminium alloy comprises more than 50% aluminium and one or more of Mg, Zn, Al and Si. Metal strips provided with aluminium  
10 coatings afford improved corrosion resistance, whereas aluminium alloys such as Al-Si alloys also improve adhesion to the metal strip and protect the metal from high temperature oxidation in high temperature applications such as hot-press forming.

In a preferred embodiment of the invention the coating material is applied by physical vapour deposition, electroplating or by hot-dip coating, preferably hot dip  
15 galvanising or by hot-dip aluminising. Although electroplating and PVD may be used to provide single sided coated metal strips, the use of hot-dip coating is preferred since the overall cost of the manufacturing process may be significantly reduced.

In a preferred embodiment of the invention the coating material comprises an organic and/or non-metallic inorganic material that is applied by roller coating or spray  
20 coating. Although it is possible to provide single sided coated metal substrates in this way, the number of single sided coated metal strips produced according to the method of the invention may be increased by a factor of two, thereby increasing the overall efficiency of the process.

In a preferred embodiment of the invention the metal strip comprises aluminium or  
25 steel. Aluminium and low carbon steel are particularly suitable for use as a skin of a metal-polymer-metal laminate. The steel may also be selected from the group consisting of dual phase steel, transformation induced plasticity steel, twinning induced plasticity steel, quenched and partitioned steel, boron steel, interstitial-free steel, bake hardenable steel and high strength low alloy steel. These steels exhibit improved  
30 strength and ductility characteristics that are particularly attractive to the automotive industry where weight reduction is becoming an increasingly important issue. A preferred steel composition comprises 0.04 - 0.30 % C, 1.0 - 3.5 % Mn, 0 - 1.0 % Si, 0 - 2.0 % Al and 0 - 1.0 % Cr. Other elements can be present, such as V, Nb, Ti and B, but usually in a small amount. The steel may also be an electrical steel for use in  
35 electrical transformers.

According to an embodiment of the invention the coated first metal strip and the coated second metal strip may be coiled. This has the advantage that the coated strips,

after separation, may be stored for future use. Alternatively the separated coated strips can be used in a subsequent manufacturing process without being coiled. For example, the coated first metal strip and the coated second metal strip may be fed into a laminating line, preferably a belt laminating line, and laminated with a polymeric layer provided therebetween. The laminate can then be coiled or blanked. Alternatively the coated metal strips can be coiled after separation and then fed into the laminating line as above.

In a preferred embodiment of the invention the metal strip stack has a width dimension of at least 1250 mm, preferably between 1250 and 2100 mm. Metal strips having such dimensions are particularly suitable for subsequent use in the automotive and construction sectors.

In a preferred embodiment of the invention the thickness of the first metal strip differs from the thickness of the second metal strip. Such an asymmetric metal strip stack is particularly advantageous when the single sided coated metal strips are to be used in the production of metal-polymer-metal laminates since the thicker of the two coated single sided coated metal strips provides improved dent resistance to the laminate.

In a preferred embodiment of the invention the thickness of the metal strip stack is reduced before and/or after coating of the metal strip stack. A metal strip stack thickness between 0.1 and 10 mm is preferred. The thickness of the stack may be reduced prior to coating the stack, which has the advantage that only a single milling operation is required to obtain the desired thickness of the first metal strip and the second metal strip. For instance, a metal strip stack having a total thickness of 1.4 mm comprising two metal strips, each having a thickness of 0.7 mm may be milled down to a stack thickness of 0.3 mm in order to obtain two 0.15 mm thick metal strips. In principle it is also possible to subject the coated stack to a single milling operation or to subject the coated first metal strip and the coated second metal strip to two separate milling operations in order to obtain the desired thickness. However, it is preferred to carry out any milling operation prior to coating the stack since the possibility of damaging the applied coating is reduced. Alternatively the thickness of the first metal strip and the second metal strip can be reduced in two separate milling operations prior to providing the metal strip stack. However, subjecting the stack to a milling operation instead of milling the first metal strip and the second metal strip independently, means the thickness of each metal strip can be reduced to a greater extent.

Preferably the thickness of the metal strip stack is reduced by cold-rolling and/or by hot-rolling.

When the metal strip stack is to be hot-dip galvanised, it is preferred to reduce the thickness of the metal strip stack before an annealing treatment that precedes hot-dip galvanising.

According to an embodiment of the invention the metal strip stack comprises a metal or metal alloy substrate situated between the first metal strip and the second metal strip. This allows the thickness of the metal strip stack to be reduced to a much greater extent relative to a stack consisting of the first metal strip and the second metal strip. A further metal strip is suitable for this purpose. The metal or metal alloy substrate may also act as a filler material that fills openings between strip edges caused by undulations, i.e. wavy regions along the strip edge. Soft metals are particularly preferred as filler substrates although suitable polymeric materials can also be used.

According to a preferred embodiment of the invention at least a portion of the first metal strip and at least a portion of the second metal strip are joined together. This may be achieved by providing an adhesive or a layer of a soft metal between at least the edges of the first metal strip and the second metal strip. Alternatively the first metal strip and the second metal strip may be welded by laser welding or resistance welding. Preferably the resistance welding is seam welding such as mash seam welding. If the first metal strip and the second metal strip are joined together by welding, then it is preferred to remove the weld after coating, preferably by slitting, to enable separation of the coated strips. Similarly, edge trimming of the coated metal strip stack or of the coated metal strips after separation may be necessary if the edges of the stack are not properly coated.

Joining the first metal strip and the second metal substrate has the advantage that zinc or zinc alloy is prevented from substantially contacting the first inner surface and the second inner surface. Moreover, water vapour in the air is prevented from being drawn between first metal strip and the second metal strip by capillary action. Thus, the potential for corrosion to occur at the first inner surface and the second inner surface is avoided or at least reduced.

In a preferred embodiment of the invention the first inner surface and/or the second inner surface is provided with a non-stick coating prior providing the metal strip stack. Although separating the coated metal strips is relatively straightforward, it may be desirable to provide an additional coating having non-stick properties to facilitate separation of the coated first metal strip and the coated second metal strip. Preferably the coating does not substantially thermally degrade when hot-dip coating the stack. Suitable non-stick materials include  $\text{SiO}_2$ .

The second aspect of the invention relates to a single sided coated metal strip produced according to the method of the first aspect of the invention, which coated metal

strip has a first major surface and a second major surface wherein the coating material is present on the first major surface and wherein at least a portion of the second major surface is not coated with the coating material.

In a preferred embodiment of the invention the thickness of the metal strip of the second aspect of the invention is between 0.08 and 2 mm, preferably between 0.1 and 0.3 mm, more preferably between 0.12 and 0.19 mm. Metal strips of the present invention having a thickness between 0.08 and 2 mm are suitable for producing products having a wide range of applications, particularly in the automotive and aerospace sectors. The above metal strips are suitable as 'skins' for use in metal-polymer-metal laminates, which laminates are suitable for automotive body work parts such as outer panels. A thickness between 0.12 and 0.19 mm is particularly suitable for this purpose.

In a preferred embodiment of the invention the coated metal strip comprises an organic coating and/or a non-metallic inorganic coating on the coating material to afford additional corrosion protection to the coated metal strip and/or to improve its aesthetic appearance. Alternatively or in addition to, the organic and/or non-metallic inorganic coating may be provided on the surface not coated with the coating material to improve adhesion, for instance, with a polymer core of a metal-polymer-metal laminate. Suitable organic coatings comprise epoxies and epoxies containing polypropylene particles, whereas preferred inorganic coatings comprise silanes, chromates and chromate free-coatings based on titanium, manganese or phosphates.

The third aspect of the invention relates to a laminate comprising a first metal skin, a second metal skin and a polymeric core layer disposed therebetween wherein the first metal skin and/or the second metal skin is formed from the coated metal strip according to the second aspect of the invention, and wherein the coating material is facing away from the polymeric core layer.

In a preferred embodiment of the invention the polymeric core layer has a thickness between 0.5 and 2.5 mm. Such a thickness is particularly suitable for automotive body work parts such as outer panels. Such panels are sufficiently rigid to satisfy body work part requirements for motor vehicles and exhibit good noise dampening properties. For metal-polymer-metal laminates it is preferred that the thickness of the first metal skin and/or the second metal skin is between 0.1 and 0.3, preferably between 0.12 and 0.19 mm.

Embodiments of the present invention will now be described by way of example. These examples are intended to enable those skilled in the art to practice the invention and do not in anyway limit the scope of the invention as defined by the claims.

Figure 1 shows a general method for manufacturing the single sided coated metal strip of the invention wherein a first metal strip (1) and a second metal strip (2)

are provided and stacked to form a metal strip stack (3). The metal strip stack is then coated by immersing the stack in a hot-dipping bath containing a molten metal or metal alloy (4). The coated stack is then removed from the bath and separated in a separating section (5) to provide two single sided metal or metal alloy coated metal strips (6). The single sided metal or metal alloy coated metal strips are then coiled at a coiler (7).

Figure 2 shows a simplified view of:

- (a) the first metal strip (1) having a first inner surface (1a) and a first outer surface (1b) and the second metal strip (2) having a second inner surface (2a) and a second outer surface (2b);
- (b) the metal strip stack (3) comprising the first metal strip and the second metal strip wherein the first inner surface and the second inner surface are facing each other and are protected from contacting the metal or metal alloy during hot-dipping;
- (c) the metal strip stack comprising the first metal strip and the second metal strip wherein the metal or metal alloy coating (8) is present on the first outer surface and the second outer surface.
- (d) The first metal or metal alloy coated metal strip and the second metal or metal alloy coated metal strip after separation.

According to an example a low carbon steel strip was cut into two 200 x 120 x 0.7 mm samples. Each steel strip was degreased in an alkaline bath and then cleaned with a suitable organic solvent such as acetone. The edges of each steel strip were then mechanically grinded before the steel sheets were stacked and subsequently spot welded along the rolling direction. The thickness of the stack was then reduced from 1.4 mm to 0.3 mm by cold rolling the stack in passes of  $\pm 0.2$  mm.

The steel stack having a reduced thickness of 0.3 mm was then annealed in accordance with a common hot-dip galvanising cycle to obtain a stack temperature of approximately 1000°C. The stack was then cooled to 440°C and subsequently hot-dip galvanised. The spot welded edges were then removed by slitting and the stacked sheets separated to obtain two single sided galvanised steel sheets having a thickness of 0.15 mm.

The inventors found that the steel stack could be easily cold rolled from 1.4 mm to 0.3 mm and that subsequent hot-dip galvanising of the stack resulted in good zinc adhesion to the steel strip. The inventors also found that the coated steel strips of the steel strip stack could be easily separated after removal of the weld to produce a first single sided galvanised steel strip and a second single sided galvanised steel strip.

**CLAIMS**

1. Method for manufacturing a coated metal strip which comprises the steps of:
- 5 (i) providing a metal strip stack comprising a first metal strip and a second metal strip, the first metal strip having a first inner surface and a first outer surface and the second metal strip having a second inner surface and a second outer surface;
- 10 (ii) providing a coating material on the metal strip stack, wherein the thickness of the metal strip stack is reduced before coating, at least the first outer surface and the second outer surface are coated with the coating material and at least a portion of the first inner surface and the second inner surface is not coated with the coating material;
- 15 (iii) separating the coated first metal strip and the coated second metal strip to provide two single sided coated metal strips.
2. Method according to claim 1, wherein the coating material is a metal or metal alloy comprising zinc, the zinc alloy comprising more than 50 % zinc and one or more of Mg, Al, Si, Mn, Cu, Fe and Cr.
- 20 3. Method according to claim 1, wherein the coating material is a metal or metal alloy comprising aluminium, the aluminium alloy comprising more than 50% aluminium and one or more of Mg, Zn, Al and Si.
- 25 4. Method according to any one of the preceding claims, wherein the coating material is applied by physical vapour deposition, electroplating or hot-dip coating, preferably hot-dip galvanising or by hot-dip aluminising.
- 30 5. Method according to claim 1, wherein the coating material is an organic and/or non-metallic inorganic material that is applied by roller coating or by spray coating.
- 35 6. Method according to any one of the preceding claims, wherein the metal strip comprises aluminium or steel, preferably the steel comprises low carbon steel, dual phase steel, transformation induced plasticity steel, twinning induced plasticity steel, quenched and partitioned steel, boron steel, interstitial-free steel, bake hardenable steel, high strength low alloy steel and electrical steel.

7. Method according to any one of claims 1-6, wherein the metal strip stack has a width dimension of at least 1250 mm, preferably between 1250 and 2100 mm.
- 5 8. Method according to any one claims 1-7, wherein the thickness of the first metal strip differs from the thickness of the second metal strip.
9. Method according to any one of claims 1-8, wherein the thickness of the metal strip stack is reduced after coating the metal strip stack.
- 10 10. Method according to any one of the preceding claims, wherein the metal strip stack comprises a metal or a metal alloy substrate between the first metal strip and the second metal strip.
- 15 11. Method according to any one of the preceding claims, wherein at least a portion of the first metal strip and at least a portion of the second metal strip are joined, preferably by an adhesive or by welding.
- 20 12. Coated metal strip produced according to the method of any one of claims 1-11, having a first major surface and a second major surface, wherein the coating material is present on the first major surface and wherein at least a portion of the second major surface is not coated with the coating material.
- 25 13. Coated metal strip metal strip of claim 12, wherein the thickness of the metal strip is between 0.08 mm and 2 mm, preferably between 0.1 and 0.3 mm, more preferably between 0.12 and 0.19 mm.
- 30 14. Coated metal strip of claim 12 or claim 13, wherein the metal strip comprises an organic coating and/or a non-metallic inorganic coating on the coating material and/or on the surface without the coating material.
- 35 15. Laminate comprising a first metal skin, a second metal skin and a polymeric core layer disposed therebetween, wherein the first metal skin and/or the second metal skin is formed from the coated metal strip according to any one of claims 12-14, and wherein the coating material is facing away from the polymeric core layer.

16. Laminate according to claim 15, wherein the polymeric core layer has a thickness between 0.5 and 2.5 mm.

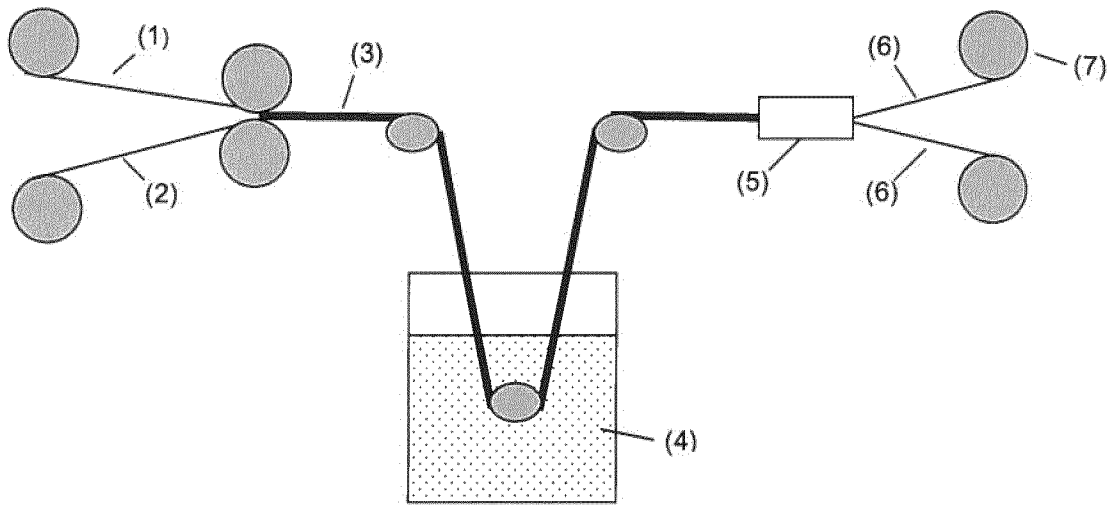


Fig.1

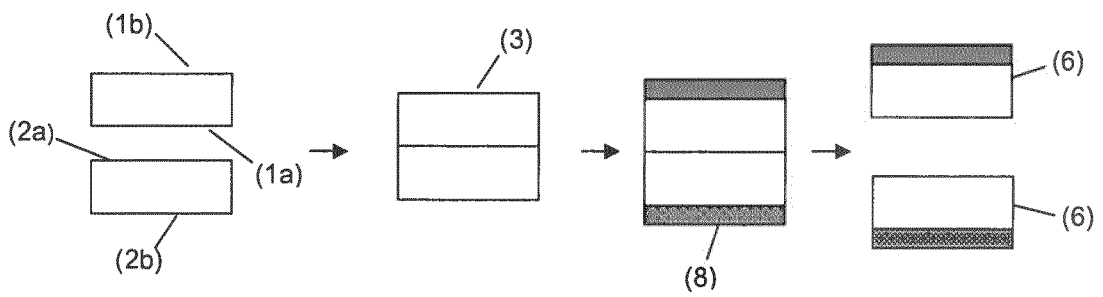


Fig.2

**INTERNATIONAL SEARCH REPORT**

International application No  
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**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C23C2/00      C23C2/02      C23C2/26      C23C2/34      C23C2/40  
 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

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**

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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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  11 July 2013	Date of mailing of the international search report  18/07/2013
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Chalaftris, Georgios
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2013/001816

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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