
A method for activating a surface of a non-conductive or carbon-fibres containing substrate for metallization

5 **Field of the Invention**

The present invention relates to the activation of surfaces of typically non-conductive or carbon-fibres containing substrates for subsequent metallization.

In particular, the present invention relates to a method for activating a surface of a non-conductive or carbon-fibres containing substrate for metallization, a method for metallizing
10 an activated surface of a non-conductive or carbon-fibres containing substrate, a method for preparing an aqueous, palladium-free activation composition for activating a surface of a non-conductive or carbon-fibres containing substrate for metallization, and an aqueous, palladium-free activation composition for activating a surface of a non-conductive or carbon-fibres containing substrate for metallization.

15 **Background of the Invention**

A metallization of typically such substrates is commercially of high interest. In many aspects of daily life such substrates are covered with structures or layers of metal, either for decorative or functional applications. For example, typically non-conductive plastic substrates are used to manufacture sanitary articles with a shiny chromium layer. Furthermore, quite a
20 number of chromium covered plastic substrates are used in the automotive industry.

Besides such decorative articles, a functional metallization is essential in for example manufacturing printed circuit boards. In such boards typically a non-conductive resin-containing laminate is used as a base material usually harboring a circuitry of copper lines.

Carbon-fibres containing substrates experience an increasing potential as catalytically active surfaces in e.g. power-to-gas, power-to-fuel, and power-to-chemicals applications, and
25 batteries.

All these applications require a usually multi-step preparation of the non-conductive or carbon-fibres containing substrate to make it receptive for subsequent metallization.

In a first step usually a cleaning of the surface of the non-conductive or carbon-fibres containing substrate is carried out, e.g. to remove grease or impurities.
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In a second step typically a conditioning (also called pre-treatment) of said surface is conducted in order to make the surface receptive to the following activation. Such a conditioning for example includes in some cases an etching in order to create pores and to enlarging the surface.

In a third step the important activation is carried out. In such an activation usually a very thin seed or activation layer is deposited/anchored on the surface of the non-conductive or carbon-fibres containing substrate, serving as starting point for a subsequent first metallization layer. As a result, an activated surface for metallization is obtained. The seed or activation layer usually serves as mediator between said surface of the non-conductive or carbon-fibres containing substrate and the one or more following metallization layers. Typically, the seed/activation layer is formed by depositing metal nanoparticles on said surface, for example from a colloidal activation composition.

In a fourth step typically said first metallization layer is deposited on the seed/activation layer, most commonly by electroless plating. In some cases, this electroless plating includes an immersion-type plating, i.e. a deposition of a more noble metal on the seed/activation layer by means of exchange reaction and in absence of a reducing agent. In other cases, it includes a deposition of a metal or metal alloy through autocatalytic deposition, which means a deposition facilitated by means of a reducing agent.

In a fifth step typically a second metallization layer is deposited on the first metallization layer, either again by autocatalytic deposition or by electrolytic deposition.

Basically, the skilled person is well familiar with such a sequence of steps. Typically, in a common colloidal activation composition, noble metal nanoparticles are utilized very often as palladium nanoparticles. However, noble metals are generally expensive and wastewater treatment is of high concern in order to recycle remaining noble metals. Alternatively, also less expensive metal ions are more and more utilized in respective activation compositions.

Another common disadvantage is that such activation compositions naturally experience a form of decay or decomposition. Typically, the nanoparticles agglomerate and form insoluble, precipitating agglomerates, rendering the composition mostly inoperable. It is therefore typically desired to stabilize the nanoparticles after they have been formed through reducing respective metal ions. For this purpose, usually stabilizer compounds are used, altering the charge distribution of the particles, limiting the particle size, and/or preventing oxidation of the particles. In many cases polymers and/or anti-oxidation agents and/or metal ions (such as tin ions) are used for these purposes.

For example, CN 107460459 A relates to simple nano-copper activation liquid utilizing stabilizers and reducing agents to prevent agglomeration and oxidation, respectively, of the nanoparticles.

CN 109295442 A relates to a method for preparing an electroless copper-nickel bimetal layer, wherein the method uses a colloidal copper activation.

US 4,278,712 discloses a method for the activation of a weakly active colloidal dispersion useful in the preparation of non-conductors prior to electroless plating. The method is based upon controlled oxidation of otherwise weakly active colloids by treatment with suitable gases and/or chemical agents, which render said controlled oxidation. However, the presence of at least one colloid stabilizer is mandatory. In this way a reversible equilibrium is not maintained.

Such approaches as described in the art typically have the disadvantage that they are sooner or later sensitive to agglomeration and precipitation, mostly because the stabilizer compounds do not sufficiently stabilize the particles over time. As a result, product lifetime very strongly depends on the date of production, delivery time, and the quality of stabilization.

Furthermore, it appears that such stabilizer compounds often reduce the ability of the nanoparticles to effectively activate the respective surface. It seems that the additives on the one hand - at least to a certain degree - avoid agglomeration but on the other hand hinder these particles to adsorb on the surface quickly and strongly.

WO 2020/201387 A1 discloses a method for activating a surface of a non-conductive or carbon-fibres containing substrate for metallization and a respective activation composition, which is on the one hand simple and highly effective, and on the other hand is in particular insensitive to agglomeration and precipitation to ensure a long service life.

It was found that metallized substrates prepared according to such a process exhibit a minor performance in the solder shock test.

Objective of the present Invention

It was therefore an objective of the present invention to provide a method for activating a surface of a non-conductive or carbon-fibres containing substrate for metallization and a respective activation composition, which is on the one hand simple and highly effective, and on the other hand is in particular insensitive to agglomeration and precipitation to ensure a long service life. Furthermore, such a method and respective composition should be low-priced.

It was another objective of the present invention to provide a respective method that exhibits a good performance in the solder shock test.

It was another objective of the present invention to provide a respective method with reduced environmental burden, e.g. with less sophisticated waste-water treatment and reduced effective concentrations of chemicals.

It was furthermore an objective of the present invention to provide a respective method with increased lifetime, in particular for the utilized activation composition.

Summary of the Invention

- The objectives mentioned above are solved by a method for treating a surface of a non-conductive or carbon-fibres containing substrate, the method comprising the steps
- (I) conditioning the surface of a non-conductive or carbon-fibres containing substrate, the conditioning method comprising the steps of
- (a) providing said substrate;
 - (b) providing a conditioning composition comprising a nitrogen-containing compound; and
 - (c) contacting the substrate with the conditioning composition;
- (II) a selector treatment of the surface of a non-conductive or carbon-fibres containing substrate, the selector treatment method comprising the steps of
- (a) providing the substrate treated according to step (I);
 - (b) providing a selector composition which
 - (i) comprises a nitrogen-containing compound; and
 - (ii) has a pH of from 9 to 14; and
 - (c) contacting the substrate (substrate treated according to step (I)) with the selector composition; and
- (III) activating the surface of a non-conductive or carbon-fibres containing substrate for metallization, the activation method comprising the steps of
- (a) providing the substrate treated according to step (II);
 - (b) providing an aqueous, palladium-free activation composition comprising
 - (i) a first species of dissolved transition metal ions and additionally metal particles thereof,
 - (ii) one or more than one complexing agent, and
 - (iii) permanently or temporarily one or more than one reducing agent, and
 - (iv) optionally one or more than one second species of dissolved metal ions being different from the first species,
- wherein

- at least of the first species, the dissolved transition metal ions and the metal particles thereof are present in a reversible equilibrium, with the proviso that
 - the metal particles are formed from the dissolved transition metal ions through a continuous or semi-continuous reduction through the one or more than one reducing agent,
 - the dissolved transition metal ions are formed from the metal particles through continuous or semi-continuous oxidation of said particles, and
 - the dissolved transition metal ions and the metal particles thereof, respectively, are repeatedly involved in said reduction and said oxidation such that no precipitating agglomerates of said metal particles are formed; and
- (c) contacting the substrate (substrate treated according to step (II)) with said activation composition such that a transition metal or a transition metal alloy is deposited on the surface of said substrate and an activated surface for metallization is obtained.

Own experiments have shown that in the present invention a very simple and effective activation is achieved even without the need of sophisticated stabilization/anti-oxidation of formed particles. In contrast to common activation compositions, it turned out that no stabilization/anti-oxidation of formed particles is needed at all. This means that in the present invention particles are not formed with the goal to maintain them as long as possible but rather to establish an equilibrium between dissolved transition metal ions and respective particles thereof, allowing the particles intentionally/purposely to re-form again and again the respective ions thereof by oxidation. Typically, in common activation compositions oxidation is considered harmful and is therefore minimized and/or suppressed. In contrast thereto, in the present invention oxidation is advantageously utilized, necessary, and considered to be of great benefit. It turned out, contrary to common thinking, that it is not necessary to maintain the particles for a long time in a respective activation composition.

This brings along a number of advantages. For example, in a very simple manner a respective activation composition is easily set up/activated at the place where it is needed by simply adding the required reducing agent. This means that product delivery time is irrelevant for the lifetime of the product/method.

The present invention relies on the fact, that the particles are formed again and again *in situ*, which renders any stabilization or stabilizer compounds obsolete. For that the dissolved transition metal ions and the metal particles thereof are present in a reversible equilibrium. As a result, a very effective and strong activation can be achieved because fresh particles

without a shell of stabilizer compounds around them are formed with a relatively short life-time. Subsequently, they are reacted back into their ionic form by oxidation. Upon adding further reducing agent fresh particles are formed again, i.e. *in situ*.

In the method of the present invention a transition metal or a transition metal alloy is deposited on the surface of said substrate and an activated surface for subsequent metallization is obtained. This means that the concentration of dissolved metal ions of the first species decreases over time due to deposition. However, replenishment of the first species is easily achieved by simply adding ions of that species. Therefore, replenishment is extremely easy and simple. This furthermore, significantly increases the lifetime of a respective activation composition and a thereto related method.

Furthermore, the respective method and activation composition does not necessarily require expensive noble metals but can be carried out with low-priced transition metals.

Detailed Description of the Invention

In the context of the present invention, “continuous”, “continuously”, and “continually”, respectively, denote a constantly ongoing doing of a respective action without significant interruptions of the action while e.g. a respective method or aspect of the invention is carried out.

In the context of the present invention, “semi-continuous”, “semi-continuously”, and, “semi-continually”, respectively, denote a doing of a respective action with one or more than one even significant interruption of the action while e.g. a respective method or aspect of the invention is carried out. The interruptions are in some cases longer than the time during the action is carried out. It includes even only temporary and brief actions.

In the context of the present invention, “species” (e.g. first species or second species) denotes a chemical element. Thus, “a first species of dissolved transition metal ions” denotes dissolved metal ions of a transition metal element of groups 3 to 12 of the periodic table, e.g. copper.

In the context of the present invention, “a first species of dissolved transition metal ions and additionally metal particles thereof” denotes dissolved metal ions of this first species and additionally metal particles of this first species, e.g. in the aqueous, palladium-free activation composition.

The substrate:

In step (I)(a) of the method of the present invention, a non-conductive or carbon-fibres containing substrate with a surface is provided. Such a substrate inherently cannot be successfully metallized and therefore needs an activation.

In the context of the present invention, activating means to modify the surface of the non-conductive or carbon-fibres containing substrate in such a way that it comprises the transition metal or transition metal alloy after the respective activation step with sufficient adhesion for subsequent metallization. Furthermore, the deposited transition metal and transition metal alloy, respectively, is sufficiently adherent to the surface such that a subsequent metallization layer (i) can be deposited thereon and (ii) is altogether also sufficiently adherent to the surface of the non-conductive or carbon-fibres containing substrate.

Preferred is a method of the present invention, wherein the non-conductive substrate comprises, preferably is, selected from the group consisting of plastics, resin-containing laminates, glasses, ceramics, semi-conductors, and mixtures thereof.

Preferred plastics comprise, preferably are, thermoplastics, more preferably comprise, preferably are, polyacrylates, polyamides, polyimides, polyesters, polycarbonates, polyalkylenes, polyphenylenes, polystyrenes, polyvinyls, or mixtures thereof.

Preferred polyacrylates comprise poly(methyl methacrylate) (PMMA).

Preferred polyimides comprise polyetherimide (PEI).

Preferred polyesters comprise polylactic acid (PLA).

Preferred polycarbonates comprise polycarbonate obtained with bisphenol A (PC).

Preferred polyalkylenes comprise polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), polyoxymethylene (POM), or mixtures thereof.

Preferred polyphenylenes comprise poly(phenylene oxide) (PPO), poly(phenylene ether) (PPE), or mixtures thereof.

Preferred polystyrenes comprise polystyrene (PS), acrylonitrile butadiene styrene (ABS), styrene/butadiene rubber (SBR), styrene-acrylonitrile (SAN).

Preferred polyvinyls comprise polyvinyl chloride (PVC), poly(ethylene-vinyl acetate) (PEVA), polyvinylidene difluoride (PVDF), or mixtures thereof.

Preferred resin-containing laminates comprise, preferably are, fiber-enforced resin-containing laminates, most preferably glass-fiber-enforced laminates.

Very preferably, the resin-containing laminates comprise as resin one or more than one polymer of epoxys, vinylesters, polyesters, amides, imides, phenols, alkylenes, sulfones, or mixtures thereof, most preferably epoxy, imides, or mixtures thereof.

A very preferred resin-containing laminate comprises, preferably is, FR4.

Preferred glasses comprise, preferably are, silica glass, soda-lime glass, float glass, fluoride glass, aluminosilicate glass, phosphate glass, borate glass, borosilicate glass, chalcogenide glass, aluminium oxide glass, or mixtures thereof.

5 Preferred ceramics comprise, preferably are, glass-ceramics, aluminium oxide ceramics, or mixtures thereof.

Preferred semi-conductors comprise, preferably are, silicon-based semi-conductors, more preferably silicon-based semi-conductors comprising silicon dioxide and/or silicon.

Very preferred semi-conductors are wafers.

10 Preferred is a method of the present invention, wherein the carbon-fibres containing substrate comprise, preferably are, carbon-fibre composites and/or arrangements of carbon-fibre filaments.

Preferred carbon-fibre composites comprise, preferably are, carbon-fibre reinforced polymers and/or carbon-fibre containing fabrics, more preferably carbon-fibre reinforced polymers and/or woven carbon-fibre containing fabrics.

15 Preferred arrangements of carbon-fibre filaments comprise, preferably are, fabrics made of carbon-fibres, most preferably woven fabrics made of carbon-fibres.

An in particularly preferred carbon-fibres containing substrate is a carbon-fibre containing felt.

20 (I) Conditioning (alternative designation: Pre-treatment):

Preferred is a method of the present invention, wherein the conditioning solution has an alkaline pH, preferably a pH in a range from 9.0 to 14.0, more preferably in a range from 10.0 to 13.5, even more preferably in a range from 10.5 to 13.0, most preferably in a range from 11.0 to 12.5.

25 Preferred is a method of the present invention, wherein in the conditioning solution the nitrogen-containing compound is a polymer, preferably a water-soluble polymer.

More preferred is a method of the present invention, wherein in the conditioning solution the nitrogen-containing compound is a polymer comprising pyrrolidine moieties.

Preferably, the polymer is cationic.

30 Preferably, the nitrogen-containing compound consists of carbon atoms, nitrogen atoms, and hydrogen atoms.

Preferred is a method of the present invention, wherein in the conditioning solution the nitrogen-containing compound comprises quaternary nitrogen atoms.

Most preferred is a method of the present invention, wherein the nitrogen-containing compound comprises, preferably is, Polyquaternium 6.

- 5 Another preferred method of the present invention is a method, wherein the nitrogen-containing compound comprises, preferably is, a polymer which results from the polyaddition and/or polycondensation of at least one nitrogen-containing compound. Examples are polyamides such as Nylon 6, Nylon 6,6, Nylon 6,16, and polyurethanes. Most preferred is a method of the present invention, wherein the nitrogen-containing compound comprises,
10 preferably is, a polymer of methylamine and epichlorohydrin.

Preferred is a method of the present invention, wherein the concentration of the nitrogen-containing compound is of from 0.1 g/L to 4 g/L, preferred of from 0.2 g/L to 2 g/L, more preferred of from 0.25 g/L to 1.5 g/L, more preferred of from 0.3 g/L to 1 g/L.

- Preferred is a method of the present invention, wherein the conditioning solution during step
15 (I)(c) has a temperature in a range from 20°C to 90°C, preferably in a range from 25°C to 80°C, more preferably in a range from 30°C to 70°C, most preferably in a range from 40°C to 60°C.

- Preferred is a method of the present invention, wherein step (I)(c) is carried out for 1 minute to 10 minutes, preferably for 2 minutes to 8 minutes, more preferably for 3 minutes to 6
20 minutes, most preferably for 3.5 minutes to 5 minutes.

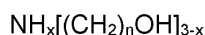
(II) Selector Treatment (alternative designation: Pre-treatment):

- Step (II) of the method of the present invention is a selector treatment of the surface of a non-conductive or carbon-fibres containing substrate, the selector treatment method comprising the steps of
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- (a) providing the substrate treated according to step (I)
- (b) providing a selector composition which
 - (i) comprises a nitrogen-containing compound; and
 - (ii) has a pH of from 9 to 14;
- 30 (c) contacting the substrate with the selector composition;

Preferred is a method of the present invention, wherein the selector composition has an alkaline pH, preferably a pH in a range from 9.0 to 14.0, more preferably in a range from 10.0 to 13.5, even more preferably in a range from 10.5 to 13.0, most preferably in a range from 11.0 to 12.5.

- 5 Preferred is a method of the present invention, wherein in the selector composition the nitrogen-containing compound is an amine of the formula



with $x = 0, 1, 2$ or 3 and

$n = 1, 2, 3$ or 4 .

- 10 More preferred is a method of the present invention, wherein in the selector composition the nitrogen-containing compound is selected from ammonia, monoethanolamine, triethanolamine, guanidine, guanidine derivatives such as guanidinium salts or mixtures thereof. In this context "guanidine derivatives" are understood as guanidine compounds, which are preferably guanidine in which one or more hydrogen is substituted by functional groups preferably as
- 15 hydroxy, halogen, amino or C1-C4 alkyl and/or wherein these guanidine compounds are chosen from guanidinium salts.

Preferred is a method of the present invention, wherein in the selector composition the concentration of the nitrogen-containing compound is of from 1 g/L to 50 g/L, preferred of from 2 g/L to 40 g/L, more preferred of from 3 g/L to 35 g/L, more preferred of from 5 g/L to 30 g/L.

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Even more preferred is a method of the present invention, wherein in the selector composition

(i) comprises

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a) a first nitrogen-containing compound which is selected from ammonia, monoethanolamine, triethanolamine or mixtures thereof; and

b) a second nitrogen-containing compound which is selected from guanidine, guanidine compounds such as guanidinium salts, or mixtures thereof; and

(ii) has a pH of from 9 to 12.

- 30 Even more preferred is a method of the present invention, wherein in the selector composition

(i) comprises

a) a first nitrogen-containing compound which is selected from ammonia, monoethanolamine, triethanolamine or mixtures thereof; and

b) a second nitrogen-containing compound which is selected from guanidine, guanidine compounds such as guanidinium salts, or mixtures thereof; and

(ii) has a pH of from 9 to 12,

wherein

in the selector composition the concentration of the first nitrogen-containing compound is of from 1 g/L to 50 g/L, preferred of from 2 g/L to 40 g/L, more preferred of from 3 g/L to 35 g/L, more preferred of from 5 g/L to 30 g/L, and

in the selector composition the concentration of the second nitrogen-containing compound is of from 1 g/L to 10 g/L, preferred of from 2 g/L to 8 g/L, more preferred of from 3 g/L to 7 g/L, more preferred of from 4 g/L to 6 g/L.

Preferred is a selector composition which

(i) comprises

a) a first nitrogen-containing compound which is selected from ammonia, monoethanolamine, triethanolamine or mixtures thereof; and

b) a second nitrogen-containing compound which is selected from guanidine, guanidine compounds such as guanidinium salts, or mixtures thereof; and

(ii) has a pH of from 9 to 12,

wherein

in the selector composition the concentration of the first nitrogen-containing compound is of from 1 g/L to 50 g/L, preferred of from 2 g/L to 40 g/L, more preferred of from 3 g/L to 35 g/L, more preferred of from 5 g/L to 30 g/L, and

in the selector composition the concentration of the second nitrogen-containing compound is of from 1 g/L to 10 g/L, preferred of from 2 g/L to 8 g/L, more preferred of from 3 g/L to 7 g/L, more preferred of from 4 g/L to 6 g/L..

Preferred is a method of the present invention, wherein the selector composition during step (II)(c) has a temperature in a range from 20°C to 90°C, preferably in a range from 25°C to 80°C, more preferably in a range from 30°C to 70°C, most preferably in a range from 40°C to 60°C.

Preferred is a method of the present invention, wherein step (II)(c) is carried out for 1 minute to 10 minutes, preferably for 2 minutes to 8 minutes, more preferably for 3 minutes to 7 minutes, even more preferably for 3.5 minutes to 6 minutes, most preferably for 4 minutes to 5.5 minutes.

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(III) The aqueous, palladium-free activation composition:

In step (III)(b) of the method of the present invention, an aqueous, palladium-free activation composition is provided.

The aqueous composition utilized in the method of the present invention is an aqueous composition, which means that water is the primary component. Thus, more than 50 wt.-% of the composition is water, based on the total weight of the aqueous composition, preferably at least 70 wt.-%, even more preferably at least 90 wt.-%, most preferably 95 wt.-% or more. Only in rare cases it is preferred that the composition comprises one or more than one solvent (other than water) that is miscible with water. However, most preferred (for ecological reasons) is a method, wherein water is the only solvent, and, thus, most preferably the composition is substantially free of or does not comprise organic solvents at all.

In the context of the present invention, the term "substantially free of or does not comprise" of a subject-matter (e.g. a compound, a chemical, a material, etc.) independently denotes that said subject-matter is not present at all ("does not comprise") or is present only in (to) a very little and non-disturbing amount (extent) without affecting the intended purpose of the invention ("substantially free of"). For example, such a subject-matter might be added or utilized unintentionally, e.g. as unavoidable impurity. "substantially free of or does not comprise" preferably denotes 0 (zero) ppm to 5 ppm, based on the total weight of e.g. the activation composition, preferably 0 ppm to 3 ppm, more preferably 0 ppm to 1.5 ppm, even more preferably 0 ppm to 1 ppm, most preferably 0 ppm to 0.5 ppm, even most preferably 0 ppm to 0.1 ppm. This principle applies likewise to other subject-matters, e.g. to the total weight of the transition metal or transition metal alloy obtained in step (III)(c) of the method of the present invention.

The activation composition has an acidic pH, a neutral pH, or an alkaline pH, preferably an acidic or neutral pH, most preferably an acidic pH.

Preferred is a method of the present invention, wherein the pH of the activation composition is in a range from ≥ 2.0 to ≤ 13.0 , preferably in a range from ≥ 3.0 to ≤ 12.0 , more preferably in a range from ≥ 4.0 to ≤ 11.0 , most preferably in a range from ≥ 4.5 to ≤ 10.0 .

In some cases, a method of the present invention is preferred, wherein the pH of the activation composition is in a range from ≥ 3.0 to ≤ 6.5 , preferably in a range from ≥ 4.0 to ≤ 6.0 . Preferably this applies with the proviso that the one or more than one reducing agent comprises a borohydride.

- 5 The pH in the activation composition is typically a result of the presence of (i) to (iv). If an adjustment of the pH is necessary, it is carried out by typical means. Preferred acids are mineral acids and organic acids. A preferred mineral acid is sulfuric acid. A preferred organic acid is the acid form of the one or more than one complexing agent. A preferred alkaline compound is an alkaline hydroxide, preferably NaOH, an alkaline carbonate, preferably so-
- 10 dium carbonate, and ammonia.

In the context of the present invention, the pH is determined at a temperature of 20°C, i.e. the defined pH is referenced to 20°C. Thus, only for the sake of pH determination the activation composition has a temperature of 20°C. This does not mean that the activation composition in itself is limited to the specific temperature of 20°C. For preferred temperatures of the activation composition see below.

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If the pH is significantly below 2 or above 13 a mostly insufficient activation is obtained. If the pH is too acidic typically acid-sensitive reducing agents decompose too quickly. On the contrary, if the pH is too alkaline, alkaline-sensitive reducing agents decompose too quickly.

The aqueous composition utilized in the method of the present invention is palladium-free.

20 Therefore, the activation composition is substantially free of or does not comprise palladium ions. This means that neither compounds comprising palladium are present nor palladium atoms/particles or palladium ions. Advantageously, the present invention is an excellent alternative to palladium-containing activation processes with identical or at least almost identical results in terms of activation.

25 Preferably, also other noble metals or at least expensive/rare metals are not necessary in the activation composition. Thus, preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise platinum ions, gold ions, silver ions, rhodium ions, ruthenium ions, and iridium ions, preferably is substantially free of or does not comprise platinum, gold, silver, rhodium, ruthenium, and iridium.

30 The aqueous composition utilized in the method of the present invention comprises (i) a first species of dissolved transition metal ions and additionally metal particles thereof.

Preferred is an activation composition, wherein said metal particles are nanoparticles. Preferably, the metal particles comprise one or more than one elemental metal (Me^0), preferably (essentially) consist of one or more than one elemental metal (Me^0).

Even more preferred is an activation composition, wherein the metal particles of the first species have a particle diameter in a range from 0.1 nm to 500 nm, preferably in a range from 0.5 nm to 200 nm, more preferably in a range from 1.0 nm to 100 nm, most preferably in a range from 3 nm to 50 nm, even most preferably in a range from 5 nm to 15 nm.

- 5 More preferred is a method of the present invention, wherein the metal particles of the first species in the activation composition are colloidal metal particles.

Thus, preferred is a method of the present invention, wherein the activation composition is a colloid, preferably a colloidal suspension. However, the activation composition is still a clear but colored solution depending on the coloring effect caused by the dissolved ions, primarily
10 of the first species.

In the activation composition said dissolved transition metal ions of the first species and said metal particles thereof form together a total amount of the metal of the first species. Preferred is a method of the present invention, wherein in the activation composition the metal ions of the first species and the metal particles thereof form a total concentration in a range from 0.05
15 g/L to 30.0 g/L, based on the total volume of the activation composition and based on an ionic, non-particular form, preferably in a range from 0.07 g/L to 18.0 g/L, more preferably in a range from 0.09 g/L to 12.0 g/L, even more preferably in a range from 0.11 g/L to 8.0 g/L, most preferably in a range from 0.15 g/L to 6.0 g/L, even most preferably in a range from 0.2 g/L to 3.0 g/L. This means that for determining said total concentration the transition metal particles
20 of the first species are considered/calculated as dissolved metal ions.

Although the method of the present invention can be basically carried out with comparatively high concentrations of the first species, it turned out that surprisingly very low concentrations are already sufficient to obtain very efficient and excellent results (see examples). This is in particular advantageous in terms of waste-water treatment and is thus cost- and ecofriendly.

- 25 Preferred is a method of the present invention, wherein the first species is copper or cobalt, preferably copper. Copper and cobalt are cost efficient metals compared to commonly used palladium but achieve sufficient activation on the surface of the non-conductive or carbon-fibres containing substrate. The aforementioned concentrations most preferably apply to copper and cobalt, most preferably to copper.

- 30 Preferred is a method of the present invention, wherein the source of dissolved copper ions is selected from the group consisting of copper sulfate, copper chloride, copper nitrate, copper fluoroborate, copper acetate, copper citrate, copper phenyl sulfonate, copper para-toluene sulfonate, and copper alkyl sulfonates. A preferred copper alkyl sulfonate is copper methane sulfonate. The most preferred copper source is copper sulfate, most preferably CuSO_4
35 * 5 H_2O .

Optionally, the aqueous, palladium-free activation composition comprises (iv) one or more than one second species of dissolved metal ions being different from the first species. Preferably, the second species is substantially free of or does not comprise alkali metals.

Preferred is a method of the present invention, wherein the one or more than one second species is selected from the group consisting of transition metals and magnesium, preferably nickel, cobalt, iron, and magnesium, preferably nickel and cobalt, more preferably nickel. With the dissolved metal ions of the second species respective transition alloys are preferably deposited in step (c) of the method of the present invention.

Preferred is a method of the present invention, wherein the one or more than one second species is substantially free of or does not comprise tin.

In addition to the first species and the optional second species, the aqueous, palladium-free activation composition comprises (ii) one or more than one complexing agent. Preferably, the one or more than one complexing agent is suitable to form complexes with the dissolved transition metal ions of at least the first species.

Preferred is a method of the present invention, wherein the one or more than one complexing agent comprises or is an organic complexing agent, preferably a carboxylic acid and/or salts thereof, more preferably a di- or tricarboxylic acid and/or salts thereof, even more preferably a tricarboxylic acid and/or salts thereof, most preferably a hydroxy tricarboxylic acid and/or salts thereof, even most preferably citric acid, structural isomers, and/or salts thereof. A preferred structural isomer is iso-citric acid and salts thereof. Most preferably, the one or more than one complexing agent defined above (including the preferred variants) is the only complexing agent in the activation composition.

Preferred is a method of the present invention, wherein in the activation composition

- the metal ions of the first species and the metal particles thereof forming together a total concentration based on the total volume of the activation composition and based on an ionic, non-particular form, and

- the one or more than one complexing agent in a total concentration are present in a molar ratio in a range from 1.0 : 0.2 to 1.0 : 100.0, preferably in a range from 1.0 : 0.5 to 1.0 : 50.0, more preferably in a range from 1.0 : 0.85 to 1.0 : 25.0, even more preferably in a range from 1.0 : 0.95 to 1.0 : 15.0, yet even more preferably in a range from 1.0 : 1.0 to 1.0 : 10.0, most preferably in a range from 1.0 : 1.1 to 1.0 : 5.0. This very preferably applies, if the one or more than one complexing agent comprises a tricarboxylic acid and/or salts thereof, more preferably a hydroxy tricarboxylic acid and/or salts thereof, most preferably citric acid, structural isomers, and/or salts thereof.

Preferred is a method of the present invention, wherein the one or more than one complexing agent in the activation composition is present in a total amount in a range from 0.01 mol/L to 0.5 mol/L, based on the total volume of the activation composition, preferably in a range from 0.015 mol/L to 0.35 mol/L, more preferably in a range from 0.02 mol/L to 0.3 mol/L, most preferably in a range from 0.023 mol/L to 0.275 mol/L.

In addition to the first species, the optional second species, and the one or more than one complexing agent, the aqueous, palladium-free activation composition comprises permanently or temporarily (iii) one or more than one reducing agent. The one or more than one reducing agent is essential for forming the metal particles from the dissolved transition metal ions of at least the first species. For that the dissolved transition metal ions are chemically reduced, continuous or semi-continuous, in order to form said particles. Thus, said particles are either formed continually or semi-continually, respectively, depending on the presence of the one or more than one reducing agent in the activation composition, which is permanent or temporary. However, when the one or more than one reducing agent is present, typically said particles will be formed until said reducing agent is used up or insufficiently present. Preferred is a method of the present invention, wherein the oxidation affects said particles and is in constant competition with the reduction. Typically, oxidation starts as soon as the one or more than one reducing agent is used up, which is explicitly desired in the context of the present invention.

Said oxidation is furthermore very relevant if in the method of the present invention after one or more than one first step (c) the method is interrupted for a comparatively long time. In order to prevent precipitating agglomerates during such a time, in the activation composition said oxidation is carried out until no particles are any longer present but rather only dissolved transition metal ions. Preferably, the oxidation is accelerated by adding an oxidizing agent, more preferably a peroxide, most preferably hydrogen peroxide. Upon resuming operation, particles are formed by adding continually or semi-continually the one or more than reducing agent to re-form particles. Afterwards, the method of the present invention is resumed.

Thus, preferably the one or more than one reducing agent is suitable for reducing the dissolved transition metal ions of at least the first species.

In some cases, preferred is a method of the present invention, wherein the one or more than one reducing agent comprises one or more than one hydrogen atom such that hydrogen is released upon reducing said transition metal ions, which at least partly adsorbs on said activated surface.

Preferred is a method of the present invention, wherein the one or more than one reducing agent comprises a boron-containing reducing agent, preferably a borohydride. A preferred

borohydride comprises an inorganic borohydride and/or an organic borohydride. A preferred organic borohydride comprises an alkylaminoborane, most preferably dimethylaminoborane. A preferred inorganic borohydride comprises an alkali borohydride, most preferably sodium borohydride. In the method of the present invention, most preferred is an alkali borohydride, preferably sodium borohydride. This allows a slightly acidic pH and a temperature in step (c) of the method of the present invention, in a moderate range, preferably from 15°C to 30°C. These are excellent room temperature conditions. Thus, no additional and cost-intensive heating is necessarily required. Furthermore, hydrogen is generated.

Preferably, the boron-containing reducing agent, preferably a borohydride, more preferably an alkali borohydride and/or an alkylaminoborane, most preferably sodium borohydride and/or dimethylaminoborane is the only reducing agent in the activation composition.

As a result of utilizing a borohydride in the activation composition as one of the one or more than one reducing agent, typically boric acid and/or salts thereof are formed.

In some cases, a method of the present invention is preferred, wherein the one or more than one reducing agent comprises an aldehyde, preferably formaldehyde, glyoxylic acid, salts of glyoxylic acid, or mixtures thereof, most preferably as the only reducing agent. In such a case formation of boric acid is avoided.

In some cases, a method of the present invention is preferred, wherein the one or more than one reducing agent comprises hydrazine, most preferably as the only reducing agent. Also, in such a case formation of boric acid is avoided.

Preferred is a method of the present invention, wherein the activation composition comprises the one or more than one reducing agent in a total concentration in a range from 0.2 mmol/L to 500.0 mmol/L, based on the total volume of the activation composition, preferably in a range from 0.4 mmol/L to 350.0 mmol/L, more preferably in a range from 0.6 mmol/L to 250.0 mmol/L, even more preferably in a range from 0.8 mmol/L to 150.0 mmol/L, most preferably in a range from 1.0 mmol/L to 80.0 mmol/L. An in particular preferred total concentration is in a range from 0.9 mmol/L to 50.0 mmol/L, very preferably in a range from 1.0 mmol/L to 30.0 mmol/L, most preferably in a range from 1.1 mmol/L to 10.0 mmol/L. Most preferably, this applies to the aforementioned preferred, more preferred, etc. reducing agents, most preferably to a borohydride.

Generally preferred is a method of the present invention, wherein in the activation composition

- the metal ions of the first species and the metal particles thereof forming together a total concentration based on the total volume of the activation composition and based on an ionic, non-particle form, and

- the one or more than one reducing agent (if semi-continually added, in the moment of addition) in a total concentration

are present in a molar ratio of more than 0.5, preferably of 1 or more, more preferably of 2 or more, even more preferably of 3 or more, most preferably of 3.5 or more. Very preferred is a molar ratio in the range from 1 to 20. Thus, in the activation composition the one or more than one reducing agent is preferably present (either permanently or temporarily) in such a total concentration that the dissolved transition metal ions of the first species are not quantitatively reduced into the respective particles. Furthermore, a method of the present invention is preferred, wherein the activation composition does not predominantly exhibit a reductive environment to prevent oxidation of the metal particles. On the contrary, as already mentioned, oxidation is required and desired. Thus, preferred is a method of the present invention, wherein the activation composition is predominantly kept in oxidizing condition to allow oxidation of the metal particles.

Particularly preferred is a method of the present invention, wherein in the activation composition

- the metal ions of the first species and the metal particles thereof forming together a total concentration based on the total volume of the activation composition and based on an ionic, non-particulate form, and
- the one or more than one reducing agent (if semi-continually added, in the moment of addition) in a total concentration

are present in a molar ratio in a range from 0.3 to 60.0, preferably in a range from 0.5 to 30.0, more preferably in a range from 1.0 to 20.0, even more preferably in a range from 1.5 to 10.0, most preferably in a range from 1.8 to 3.0.

In some cases, a method of the present invention is preferred, wherein in the aqueous, palladium-free activation composition the one or more than one reducing agent is permanently present. Thus, preferred is that the one or more than one reducing agent is added to the activation composition continually, preferably by a permanent flow of a respective liquid containing said one or more than one reducing agent. In this approach oxidation and reduction are taking place simultaneously over the time during step (c) of the method of the present invention is carried out. As a result, the metal particles are present in a comparatively constant concentration.

Alternatively, a method of the present invention is preferred, wherein in the aqueous, palladium-free activation composition the one or more than one reducing agent is temporarily present. Thus, preferably the one or more than one reducing agent is added semi-continuously; e.g. in consecutive portions with time-wise interruptions between each portion. This means

that when the one or more than one reducing agent is added fresh particles are formed. However, during the interruptions the oxidation, creating the dissolved transition metal ions, is very dominant. As a result, the metal particles are present in a basically varying concentration. However, depending on the length of the time-wise interruptions and making sure that the interruptions are not too long, such an approach is fully sufficient to successfully activate surfaces of even a plurality of non-conductive or carbon-fibres containing substrates. Therefore, this approach is in particular preferred.

However, in either case preferred is a method of the present invention, wherein the one or more than one reducing agent is present in such a way that the equilibrium remains reversible. Thus, the reversible equilibrium is not only a side reaction or an undesired side reaction.

Upon oxidation, in the activation composition the total concentration of the dissolved transition metal ions basically increases as a result of the reversible equilibrium, wherein the total amount of said metal particles decreases. This reversible equilibrium is preferably monitored for a better process control. Therefore, preferred is a method of the present invention, wherein the reversible equilibrium is monitored by UV/VIS inspection. Preferably, said dissolved transition metal ions are monitored at a wavelength within a range from 700 nm to 800 nm, preferably within a range from 710 nm to 780 nm, more preferably within a range from 720 nm to 760 nm, most preferably within a range from 730 nm to 750 nm. Also preferred is that said metal particles are monitored at a wavelength within a range from 400 nm to 600 nm, preferably within a range from 450 nm to 550 nm. This allows determining when to add one of the one or more than one reducing agent in order to form, preferably re-form, said metal particles in order to increase their total amount.

Thus, preferred is a method of the present invention, wherein the one or more than one reducing agent is continually or semi-continually added to the activation composition such that further metal particles are continually or semi-continually, respectively, formed from the dissolved transition metal ions of the first species, preferably added after one or more than one step (c) is carried out.

Preferred is a method of the present invention, wherein the metal particles of the first species are continually or semi-continually formed *in situ* in the activation composition by said reduction after and/or during one or more than one step (c) is carried out. This preferably defines that in the method of the present invention step (c) is carried out more than one time, preferably the method, including step (c), is carried out repeatedly. It is very preferred that after one, more than one, or each step (c) of the method of the present invention metal particles are freshly formed by said reduction. This is possible because said oxidation is allowed and desired, leading, preferably continually but at least semi-continually, to fresh dissolved transition metal ions ready for re-reduction. This is contrary to common approaches, wherein metal

particles are formed (and stabilized) before the activation is carried out, which afterwards typically last as long as possible by particle stabilization until the respective activation composition is unstable and inoperable.

As mentioned throughout the text, in the context of the present invention it is preferably necessary to add at least semi-continually a reducing agent. Typically, the reducing agent used for said reduction reacts with the dissolved transition metal ions and leads to a reducing agent degradation product, preferably boric acid and/or salts thereof. Usually, such degradation products accumulate in the activation composition, which is not preferred in the context of the present invention. Therefore, a method of the present invention is preferred, wherein the method is performed by bleed and feed. In such an approach, a certain volume of the activation composition is removed (e.g. by drag out; thereby removing also degradation products) and replaced by a replacement volume (e.g. by means of replenishment) in such a way that essential components in the activation composition have a sufficiently constant concentration. This means that the replacement volume typically does not comprise boric acid and/or salts thereof, preferably does not comprise the reducing agent degradation product. This is also beneficial for stabilizing the pH to a basically constant pH.

Preferred is a method of the present invention, wherein the activation composition comprises boric acid and/or salts thereof in a total concentration of 5 g/L or less, based on the total volume of the activation composition, preferably of 3 g/L or less, more preferably of 2 g/L or less, most preferably of 1.2 g/L or less. This preferably applies with the proviso that (1) the one or more than one reducing agent comprises a borohydride and (2) step (c) is carried out more than one time.

Preferred is a method of the present invention, wherein the reversible equilibrium is not predominantly shifted to the metal particles over the majority of time during which step (c) is carried out.

Preferred is a method of the present invention, wherein during and/or after step (c) the majority of said metal particles is subjected to said oxidation. Majority preferably denotes more than 50% of the particles.

Preferably, the one or more than one reducing agent is substantially free of or does not comprise hypophosphite ions, preferably is substantially free of or does not comprise a phosphorous-containing reducing agent. Own experiments have shown that in some cases the activation with such reducing agents is too weak or even incomplete.

As already outlined above, the activation composition does not additionally require stabilizing compounds. Therefore, preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise a compound preventing the oxidation

of the metal particles and/or is substantially free of or does not comprise a stabilizer compound to stabilize the metal particles. Preferably, the activation composition is substantially free of or does not comprise a stabilizer compound to stabilize the metal particles by preventing agglomeration of the metal particles. In the context of the present invention, the one or more than one reducing agent (temporarily or permanently present in the activation composition) and compounds involved in the oxidation, preferably ambient air and/or oxygen gas (i.e. most preferably molecular oxygen), are not considered to be such a compound. The one or more than one reducing agent is rather required in order to form the metal particles, which includes re-forming the particles. This means that the activation composition is substantially free of or does not comprise in addition to said one or more than one reducing agent and compounds involved in the oxidation a stabilizer compound and/or a compound preventing the oxidation of the metal particles. Thus, preferred is a method of the present invention, wherein the one or more than one reducing agent is not present in a total amount to prevent the oxidation, preferably is not present in a total amount to prevent the oxidation after or during one or more than one step (c) is carried out. As outlined, the oxidation, most preferably through ambient air, is needed to re-form the dissolved transition metal ions such that no precipitating agglomerates of said metal particles are formed.

A method of the present invention is preferred, wherein the activation composition is substantially free of or does not comprise a compound encapsulating fully or partly the metal particles or which fully or partly adsorbs onto the surface of the particles. It is believed that some stabilizer compounds are based on such a function. In the context of the present invention this is not desired.

Generally, a method of the present invention is preferred, wherein the activation composition is substantially free of or does not comprise a compound preventing the equilibrium from being reversible and/or is substantially free of or does not comprise a compound in order to shift the equilibrium entirely towards the metal particles. Again, the one or more than one reducing agent is not considered to be such a compound for the reasons outlined above.

Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise tin ions, preferably is substantially free of or does not comprise tin ions, lead ions, germanium ions, gallium ions, antimony ions, bismuth ions, and aluminium ions, more preferably is substantially free of or does not comprise metal ions of main groups III, IV, and V of the periodic table of elements. In the context of the present invention "metal ions of main group III" does not include respective boron-containing ions. In particular tin ions are very well known to prevent oxidation of for example copper particles in respective

palladium-free copper-tin activation compositions, thereby preventing the equilibrium from being reversible. Such tin ions typically form a reductive environment, which is by no means desired in the context of the present invention.

Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise polyvinylpyrrolidone, preferably is substantially free of or
5 does not comprise a polyvinyl compound, more preferably is substantially free of or does not comprise an organic polymer comprising a vinyl moiety, most preferably is substantially free of or does not comprise a dissolved organic polymer.

Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise a protein, agar, gum Arabic, sugars, and polyalcohols.
10

Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise glycerol.

Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise gelatin.

15 Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise thiourea, preferably is substantially free of or does not comprise sulfur-containing compounds with divalent sulfur, more preferably is substantially free of or does not comprise sulfur-containing compounds with sulfur in an oxidation number of +5 or below.

20 Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise a compound comprising an aromatic ring and a sulfonic acid group (including salts thereof), preferably is substantially free of or does not comprise a sulfonic acid or salts thereof.

Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise a compound named Orzan-S.
25

Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise urea.

Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise a dispersing agent.

30 Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise polyethylenimine, preferably is substantially free of or does not comprise polyalkylenimine, most preferably is substantially free of or does not comprise an organic polymer comprising an imine moiety.

In particular polymers as mentioned above are commonly used as stabilizer compounds in order to stabilize the metal particles. However, polymers are not necessary in the context of the present invention. Furthermore, it is believed that the metal particles are significantly more effective / more active if no such molecules are forming a shell around the particles.

5 Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise sodium dodecyl sulfate, preferably is substantially free of or does not comprise an alkyl sulfate with 8 to 20 carbon atoms, more preferably is substantially free of or does not comprise an alkyl sulfate, most preferably is substantially free of or does not comprise a surfactant.

10 Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise a hydroquinone, pyrogallol, and/or resorcinol, preferably is substantially free of or does not comprise a hydroxy benzene. In many cases such hydroxy benzenes are commonly used as anti-oxidizing agents, thereby preventing the equilibrium from being reversible, which are not needed in the activation composition.

15 Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise a quinone.

Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise a fatty alcohol.

20 Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise an alkylene glycol, preferably is substantially free of or does not comprise a glycol.

Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise manganese ions.

25 Preferred is a method of the present invention, wherein the activation composition is substantially free of or does not comprise zinc ions.

As a result and in particular despite the fact that the activation composition does not comprise a stabilizing compound and/or a compound preventing the oxidation of the metal particles, a method of the present invention is preferred, wherein the activation composition is substantially free of or does not comprise precipitating agglomerates of said metal particles. This is
30 achieved because the oxidation is not suppressed (i.e. is not avoided) but rather the dissolved transition metal ions of at least the first species and the metal particles thereof, respectively, are repeatedly involved in said reduction and said oxidation.

Preferred is a method of the present invention, wherein "repeatedly involved" explicitly includes at least more than once, preferably more than twice, even more preferably more than

three times, most preferably more than four times, even most preferably over the entire life-time of the activation composition.

Own experiments have shown that it is in particular the oxidation that prevents agglomeration. The metal particles are oxidized back into their ionic/dissolved form. This means that there is not sufficient time for the particles to form higher aggregates and to even form agglomerates. Although each suitable oxidation agent is basically applicable, ambient air proved to be an excellent choice. It is sufficiently strong and ubiquitous available. Preferred is a method of the present invention, wherein the forming of precipitating agglomerates of said metal particles is prevented through said oxidation, preferably through oxidation by ambient air and/or oxygen gas. Preferred is a method of the present invention, wherein the dissolved transition metal ions are formed from the metal particles through oxidation by ambient air and/or oxygen gas. In both cases the preferred oxidizing agent is molecular oxygen. Most preferred is a method of the present invention, wherein the majority of the dissolved transition metal ions are formed from the majority of the metal particles through oxidation by ambient air and/or oxygen gas.

In some cases, a method of the present invention is preferred, wherein the continuous or semi-continuous oxidation is additionally or solely achieved through an oxidizing agent, which is not molecular oxygen, more preferably through a peroxide, most preferably hydrogen peroxide. In particular in addition to ambient air this preferably accelerates the oxidation of the particles if this is required, e.g. if an activation composition must be inactivated and stored for longer times.

In order to sufficiently facilitate the oxidation in the activation composition, preferred is a method of the present invention, wherein the activation composition continually or semi-continually circulates, preferably by shaking, stirring and/or pumping. This is preferred to ensure that the oxidation is equally distributed in the entire activation composition. In other words, this ensures that the metal particles are equally contacted with an oxidizing agent, which facilitates the oxidation.

Very most preferred is method (for activating) a surface of a non-conductive or carbon-fibres containing substrate for metallization, the method comprising the steps

(a) providing said substrate,

(b) providing an aqueous, palladium-free activation composition comprising

(i) a first species of dissolved transition metal ions and additionally colloidal metal particles thereof, wherein the first species is copper,

- (ii) one or more than one complexing agent comprising a hydroxy tricarboxylic acid and/or salts thereof, preferably citric acid, structural isomers, and/or salts thereof,
- (iii) permanently or temporarily one or more than one boron-containing reducing agent, preferably a borohydride,
- (iv) optionally one or more than one second species of dissolved metal ions being different from the first species, wherein the second species preferably is nickel,
- wherein
- the activation composition is a colloidal suspension, and
 - at least of the first species, the dissolved transition metal ions and the metal particles thereof are present in a reversible equilibrium, with the proviso that
 - the metal particles are formed from the dissolved transition metal ions through a continuous or semi-continuous reduction through the one or more than one reducing agent,
 - the dissolved transition metal ions are formed from the metal particles through continuous or semi-continuous oxidation of said particles through oxidation by ambient air,
 - the dissolved transition metal ions and the metal particles thereof, respectively, are repeatedly involved in said reduction and said oxidation such that no precipitating agglomerates of said metal particles are formed, and
- (c) contacting the substrate with said activation composition such that a transition metal or a transition metal alloy is deposited on the surface of said substrate and an activated surface for metallization is obtained, wherein the metal particles are continually or semi-continually formed *in situ* in the activation composition by said reduction after and/or during one or more than one step (c) is carried out.

The present invention is also directed to a method for preparing an aqueous, palladium-free activation composition for activating a surface of a non-conductive or carbon-fibres containing substrate for metallization (preferably an activation composition as utilized in the method of the present invention), the method comprising the steps

- (1) providing an aqueous starting solution comprising
- a first species of dissolved transition metal ions, and

- one or more than one complexing agent, and
- optionally one or more than one second species of dissolved metal ions being different from the first species,

5 (2) continually or semi-continually adding one or more than one reducing agent to the starting solution such that metal particles of at last the first species of dissolved transition metal ions are continually or semi-continually, respectively, formed in the solution,

with the proviso that said metal particles are continually or semi-continually oxidized to form dissolved transition metal ions of the first species, wherein the method is used to provide the aqueous, palladium-free activation composition according to any of the claims 1 -10.

With other words, this method for preparing an aqueous, palladium-free activation composition for activating a surface of a non-conductive or carbon-fibres is used for providing an aqueous, palladium-free activation composition according to the present invention.

15 The aforementioned, regarding the method of the present invention, preferably applies likewise to the method of the present invention for preparing the aqueous, palladium-free activation composition, most preferably as aforementioned defined as being preferred.

The present invention is also directed to the use of continuous or semi-continuous reduction of dissolved transition metal ions of a first species in combination with continuous or semi-continuous oxidation of metal particles of the first species in a reversible equilibrium to continually or semi-continually form *in situ* metal particles in an aqueous, palladium-free activation composition.

The aforementioned, regarding the method of the present invention, preferably applies likewise to the use of the present invention, most preferably as aforementioned defined as being preferred.

The present invention is also directed to an aqueous, palladium-free activation composition for activating a surface of a non-conductive or carbon-fibres containing substrate for metallization, the composition comprising

- 30 (i) a first species of dissolved transition metal ions and additionally metal particles thereof,
- (ii) one or more than one complexing agent,
- (iii) permanently or temporarily one or more than one reducing agent,

- (iv) optionally one or more than one second species of dissolved metal ions being different from the first species,

wherein

- at least of the first species, the dissolved transition metal ions and the metal particles thereof are present in a reversible equilibrium, with the proviso that
 - the metal particles are formed from the dissolved transition metal ions through a continuous or semi-continuous reduction through the one or more than one reducing agent,
 - the dissolved transition metal ions are formed from the metal particles through continuous or semi-continuous oxidation of said particles, and
 - the dissolved transition metal ions and the metal particles thereof, respectively, are repeatedly involved in said reduction and said oxidation such that no precipitating agglomerates of said metal particles are formed.

The aforementioned, regarding the method of the present invention, preferably applies likewise to the aqueous, palladium-free activation composition of the present invention, most preferably as aforementioned defined as being preferred.

Preferably, the activation composition of the present invention is obtained at and/or has a temperature in a range from 10°C to 90°C, preferably in a range from 14°C to 75°C, more preferably in a range from 16°C to 65°C, most preferably in a range from 18°C to 45°C, even most preferably in a range from 20°C to 32°C. In particular preferred is a temperature in a range from 18°C to 45°C, preferably in a range from 20°C to 32°C, with the proviso that the one or more than one reducing agent is a borohydride, preferably sodium borohydride. This in particular preferably also applies to the method of the present invention (for preparing said activation composition) and the method of the present invention.

More preferably, the activation composition of the present invention is not obtained at and/or has not a temperature above 110°C, preferably above 100°C, more preferably above 95°C. Most preferably the activation composition of the present invention is not obtained at a temperature above 110°C. This likewise preferably applies to the method of the present invention (for preparing said activation composition) and the method of the present invention.

The activation (Step (III)):

In step (III)(c) of the method of the present invention, the substrate is contacted with the aqueous, palladium-free activation composition in order to obtain an activated surface for metallization by depositing the metal or metal alloy, i.e. depositing a seed or activation layer.

Preferred is a method of the present invention, wherein in step (III)(c) the contacting is carried out at a temperature in a range from 10°C to 90°C, preferably in a range from 14°C to 75°C, more preferably in a range from 16°C to 65°C, most preferably in a range from 18°C to 45°C, even most preferably in a range from 20°C to 32°C. In particular preferred is a temperature in step (III)(c) in a range from 18°C to 45°C, preferably in a range from 20°C to 32°C, and wherein the reduction through the one or more than one reducing agent is a borohydride, preferably sodium borohydride.

Preferred is a method of the present invention, wherein in step (III)(c) the contacting is carried out for a time in a range from 1 minute to 10 minutes, preferably for 2 minutes to 8 minutes, more preferably for 3 minutes to 6 minutes, most preferably for 3.5 minutes to 5 minutes.

Preferred is a method of the present invention, wherein after step (III)(c) a rinsing step is carried out. In such a case a rinsed, activated surface for metallization is obtained. Preferably, the rinsing is carried out with water.

Preferred is a method of the present invention, wherein the method is carried out for 10 days or more, without replacing the majority of the activation composition in one step (i.e. more than 50 vol.-% of the composition), preferably 50 days or more, more preferably 200 days or more, even more preferably 1 year or more, most preferably 2 years or more, even most preferably 5 years or more.

The metallization:

The present invention furthermore refers to a method for metallizing an activated surface of a non-conductive or carbon-fibres containing substrate, the method comprising the steps

- (A) providing the non-conductive or carbon-fibres containing substrate with the activated surface for metallization obtained by the method of the present invention, preferably as defined throughout the text as being preferred; and
- (B) metallizing the activated surface by contacting the activated surface with a first metallizing solution such that a first metallization layer is deposited on the activated surface.

In step (A) of the method of the present invention (for metallizing) the non-conductive or carbon-fibres containing substrate with the activated surface is provided as obtained by the method of the present invention; for details see text above. The aforementioned, regarding the method of the present invention, preferably applies to the method of the present invention for metallization, most preferably as described as being preferred.

Preferred is a method of the present invention (for metallizing), wherein in step (B) the first metallization layer is a distinct layer deposited on the transition metal or transition metal alloy obtained in step (III)(c) of the method of the present invention.

Preferred is a method of the present invention (for metallizing), wherein in step (B) the first metallization solution is essentially free of or does not comprise a reversible equilibrium between metal ions and particles thereof; more preferably is essentially free of or does not comprise metal/metal alloy particles, most preferably is essentially free of or does not comprise any particles.

Preferred is a method of the present invention (for metallizing), wherein in step (B) the first metallization solution comprises a reducing agent or does not comprise a reducing agent.

Preferred is a method of the present invention (for metallizing), wherein step (B) is carried out at a temperature in a range from 10°C to 95°C, preferably in a range from 15°C to 85°C, more preferably in a range from 20°C to 65°C, even more preferably in a range from 25°C to 55°C, most preferably in a range from 30°C to 45°C.

Preferred is a method of the present invention (for metallizing), wherein step (B) is carried out for 30 seconds to 180 minutes, preferably for 45 seconds to 120 minutes, more preferably for 1 minutes to 60 minutes, most preferably for 1.5 minutes to 45 minutes.

Preferred is a method of the present invention (for metallizing), wherein in step (B) the first metallization solution does not comprise a reducing agent and is an immersion type metallization solution, preferably comprising one or more than one species of ions selected from the group consisting of palladium ions, platinum ions, silver ions, gold ions, and mercury ions, more preferably comprising palladium ions, most preferably comprising palladium ions in a total concentration in a range from 0.05 mg/L to 20 mg/L.

More preferred is a method of the present invention (for metallizing), wherein in step (B) the first metallization solution is an acidic palladium immersion type metallization solution.

Preferred is a method of the present invention (for metallizing), wherein in step (B) the first metallization solution is an immersion type metallization solution comprising palladium ions in a total concentration in a range from 0.09 mg/L to 10.0 mg/L, based on the total volume of the metallization solution, preferably in a range from 0.1 mg/L to 5.0 mg/L, more preferably in a range from 0.12 mg/L to 3.0 mg/L, even more preferably in a range from 0.15 mg/L to 2.0 mg/L, most preferably in a range from 0.2 mg/L to 1 mg/L, even most preferably in a range from 0.22 mg/L to 0.75 mg/L. This particularly applies if the metallization solution is acidic. In combination with the method of the present invention, such a metallization solution

surprisingly requires a significantly low concentration of palladium ions compared to conventional prior art metallization solutions but in the context of the present invention without compromising the metallization result/quality.

Alternatively preferred is a method of the present invention (for metallizing), wherein in step
5 (B) the first metallization solution comprises a reducing agent and is an autocatalytic type metallization solution, preferably comprising one or more than one species of transition metal ions, more preferably comprising copper ions and/or nickel ions.

However, irrespective of what type the first metallization solution is, preferably it is a clear solution without particles.

10 Preferred is a method of the present invention (for metallizing) comprising the steps

- (A) providing the non-conductive or carbon-fibres containing substrate with the activated surface for metallization obtained by the method of the present invention, preferably as defined throughout the text as being preferred,
- (B) metallizing the activated surface by contacting the activated surface with a first
15 metallizing solution being an autocatalytic type metallization solution comprising copper ions and a reducing agent such that a first metallization layer comprising copper or a copper alloy is deposited on the activated surface.

Alternatively preferred is a method of the present invention (for metallizing) comprising the steps

- 20 (A) providing the non-conductive or carbon-fibres containing substrate with the activated surface for metallization obtained by the method of the present invention, preferably as defined throughout the text as being preferred,
- (B) metallizing the activated surface by contacting the activated surface with a first metallizing solution being an immersion type metallization solution comprising
25 palladium ions (preferably as described before) such that a first metallization layer comprising palladium is at least partly deposited on the activated surface, and subsequently
- (C) metallizing the first metallization layer by contacting the first metallization layer with a second metallizing solution such that a second metallization layer is de-
30 posited on the first metallization layer.

Preferred is a method of the present invention (for metallizing), wherein in step (C) the second metallizing solution comprises a reducing agent, preferably comprises a reducing agent and nickel ions.

Thus, preferred is a method of the present invention (for metallizing), wherein in step (C) the second metallization layer comprises nickel; preferably is a nickel or a nickel alloy layer.

However, in other cases preferred is a method of the present invention (for metallization), wherein in step (C) the second metallizing solution comprises a reducing agent, preferably
5 comprises a reducing agent and copper ions.

Thus, preferred is a method of the present invention (for metallizing), wherein in step (C) the second metallization layer comprises copper; preferably is a copper or a copper alloy layer.

In other cases, preferred is a method of the present invention (for metallization), wherein in step (C) the second metallizing solution comprises a reducing agent, preferably comprises
10 a reducing agent and cobalt ions.

Thus, preferred is a method of the present invention (for metallizing), wherein in step (C) the second metallization layer comprises cobalt; preferably is a cobalt or a cobalt alloy layer.

Preferred is a method of the present invention (for metallizing), wherein in step (C) the second metallization layer starts deposition within 8 seconds to 30 seconds, preferably within
15 10 seconds to 25 seconds, most preferably within 12 seconds to 20 seconds. This most preferably applies if the second metallization layer comprises nickel; preferably is a nickel or a nickel alloy layer. Thus, own experiments have shown that a first metallization layer comprising palladium functions as a booster for a second metallization layer of nickel or a nickel alloy.

20 The present invention is described in more detail by the following non limiting examples.

Examples

Test methods:

Backlight test (metal coverage on a substrate surface):

The coverage is evaluated using an industry standard Backlight test, in which the respective
25 substrate is sectioned, so as to allow areas of incomplete coverage to be detected as bright spots when viewed over a strong light source (compare US 2008/0038450 A1 and WO 2013/050332). The quality of the coverage is determined by the amount of light that is observed under a conventional optical microscope. The results are given on a scale from D1 to D10, wherein D1 (little, incomplete coverage) means the worst result and D10 (com-
30 plete, strong coverage) the best result.

Solder shock test:

Following electroless copper plating, the electrical reliability coupons were immersed for 10 s in a 10% H₂SO₄ solution at room temperature and then 40 µm of copper were electrolytically plated onto the coupons. The coupons were then annealed for 6 hours at 140 °C and, after cooling to room temperature, were subjected to a solder shock test, in which the coupons were floated for 10 s on molten solder at 288 °C and then allowed to cool to room temperature again. This floating and cooling procedure was repeated a further five times.

Peel strength:

The electrolessly plated ABF coupons were immersed for 10 s in a 10% H₂SO₄ solution at room temperature and then electrolytically plated with 35 µm of copper. After plating, the coupons were fully cured according to the Ajinomoto recommendations. The coupons were then cut into strips of 1 cm width using a routing machine. The force required to peel the copper film from these strips was measured using an Erichsen Unimat Plus 050-2kN material testing machine equipped with a 20 N load cell, at a peeling speed of 50.8 mm/min while ensuring a peeling angle of 90° at all times.

Test coupons

Acrylonitrile butadiene styrene (ABS), FR4 and laminated Ajinomoto build-up film (ABF) GX-92R test coupons (Table 1) were used for the assessment of the quality of the electroless copper deposit. The parameters tested were appearance, blistering, deposit thickness, coverage, electrical reliability and peel strength.

Table 1

Material Name	Material Type	Desmeared	Test Parameter
Metak	ABS	Yes ^a	Appearance; Blistering
Panasonic MC100EX	Bare FR4 ^b	No	Appearance; Deposit thickness
NanYa NP140	Copper-clad FR4 ^c	Yes ^a	Coverage
Isola IS410	Copper-clad FR4 ^{c,d}	Yes ^a	Coverage; Electrical reliability
GX-92R	ABF laminated on FR4 ^e	Yes ^a	Appearance; Peel strength

^aDesmear conditions are given in the relevant subsection below.

^bUnstructured and no copper inner layers.

^cCoverage coupons: 1 mm through holes without copper inner layers.

^dElectrical reliability coupons: 1 mm through holes with copper inner layers.

5 ^eLamination conditions are given in the relevant subsection below.

ABF Lamination Conditions

ABF GX-92R prepregs were laminated onto Bondfilm[®]-treated copper-clad FR4 panels using a Dynachem VA 7124-HP6 vacuum laminator (lamination conditions: 30 s vacuum time, 10 30 s dynamic slap-down time, 20 s static slap-down time, 2.0 mbar vacuum set point, 5.0 kg/cm² pressure). The laminated panels were then semi-cured in an air-circulated oven according to the Ajinomoto recommendations.

Desmear Conditions

15 Coupons requiring desmear were desmeared using the Securiganth[®] series of treatment baths listed in Table 2.

Table 2

Step ^a	Bath	Immersion Time [s]
1	Securiganth [®] MV Sweller	120 (ABS); 300 (FR4, ABF)
2	Securiganth [®] MV P-Etch	240 (ABS); 600 (FR4); 1200 (ABF)
3	Securiganth [®] MV Reduction Cleaner	120 (ABS); 300 (FR4, ABF)

^aTap water rinse of approximately 60 s between each step.

20

Inventive Example

Coupons were processed according to the conditions detailed in Table 3

25

Table 3

Step ^a	Bath	Conditions	Immersion Time [s]
1	Securiganth® MV Cleaner PF	Typical ^b	240
2	Neoganth® MV Etch Cleaner SPS	Typical ^b	60
3	Conditioner	1.69 g/L Superfloc C-521 pH 11.5; 45 °C	240
4	Selector	29.01 g/L monoethanolamine 4.54 g/L guanidinium carbonate pH 11.5; 55 °C	300
5	Activator	6.64 g/L CuSO ₄ •5H ₂ O 12.78 g/L citric acid 0.21 g/L NaBH ₄ pH 4.5; 30 °C	240
6	Printoganth® MV Plus Electroless Copper	Typical ^b	1200

^aTap water rinse of approximately 60 s between each step.

^bOperating parameters are known to the one skilled in the art.

5 The following results were yielded:

- Electroless copper deposit appearance: salmon pink, blister-free
- Deposit thickness: 1 µm
- Backlight test performance: D9-D10
- Solder shock test performance: 0% interconnect defects (ICDs) following sixfold
shocking (10 seconds each) at 288 °C
- Peel strength: 8 N/cm

10

Comparative Example 1 (Commercial palladium-based method)

Coupons were processed according to the conditions detailed in Table 4, which are representative of a commercially used palladium-based process.

5 Table 4

Step ^a	Bath	Immersion Time [s]
1	Securiganth® MV Cleaner PF	240
2	Neoganth® MV Etch Cleaner SPS	60
3	Neoganth® MV Pre Dip	60
4	Neoganth® MV Activator	240
5	Neoganth® MV Reducer S	180
6	Printoganth® MV Plus Electroless Copper	1200

^aTap water rinse of approximately 60 s between each step, except between steps 3 and 4.

The following results were yielded:

- Electroless copper deposit appearance: salmon pink, blister-free
- 10 • Deposit thickness: 1 µm
- Backlight test performance: D9-D10
- Solder shock test performance: 0% ICDs following sixfold shocking (10 seconds each) at 288 °C
- Peel strength: 8 N/cm

15

Comparative Example 2 (Palladium-free method with acidic acidic selector treatment)

Coupons were processed according to the conditions detailed in Table 5, i.e. under same conditions as the Inventive Example but with an acidic selector treatment.

20

Table 5

Step ^a	Bath	Conditions	Immersion Time [s]
1	Securiganth® MV Cleaner PF	Typical ^b	240
2	Neoganth® MV Etch Cleaner SPS	Typical ^b	60
3	Conditioner	1.69 g/L Superfloc C-521 pH 11.5; 50 °C ^c	240
4	Selector	25 g/L sodium persulfate 25g/L sodium hydrogen sulfate pH 2; 30 °C ^c	240
5	Activator	6.64 g/L CuSO ₄ ·5H ₂ O 12.78 g/L citric acid 0.21 g/L NaBH ₄ pH 4.5; 30 °C ^c	240
6	Printoganth® MV Plus Electroless Copper	Typical ^b	1200

^aTap water rinse of approximately 60 s between each step.

^bOperating parameters are known to the one skilled in the art.

5 The following results were yielded:

- Electroless copper deposit appearance: salmon pink, blister-free
- Deposit thickness: 1 µm
- Backlight test performance: D5-D7

Due to the poor backlight test performance, solder shock and peel strength test performance was not examined.

10

Comparative Example 3 (Palladium-based method)

Coupons were processed according to the conditions detailed in Table 6.

Table 6

Step ^a	Bath	Conditions	Immersion Time [s]
1	Securiganth® MV Cleaner PF	Typical ^b	240
2	Neoganth® MV Etch Cleaner SPS	Typical ^b	60
3	Conditioner	1.69 g/L Superfloc C-521 pH 11.5; 45 °C	240
4	Selector	29.01 g/L monoethanolamine 4.54 g/L guanidinium carbonate pH 11.5; 55 °C	300
5	Neoganth® MV Pre Dip	Typical ^b	60
6	Neoganth® MV Activator	Typical ^b	240
7	Neoganth® MV Reducer S	Typical ^b	180
8	Printoganth® MV Plus Electroless Copper	Typical ^b	1200

^aTap water rinse of approximately 60 s between each step, except between steps 5 and 6.

^bOperating parameters are known to the one skilled in the art.

The following results were yielded:

- Electroless copper deposit appearance: salmon pink, blister-free
- Deposit thickness: 1 µm
- Backlight test performance: D9

- Solder shock test performance: 9% ICDs following sixfold shocking (10 seconds each) at 288 °C

Due to the relatively poor solder shock test performance, peel strength test performance was not examined.

5

Comparative Example 4 (Palladium-based method)

Coupons were processed according to the conditions detailed in Table 7, i.e. under same conditions as Comparative Example 3 but without Pre-dip.

10 Table 7

Step ^a	Bath	Conditions	Immersion Time [s]
1	Securiganth® MV Cleaner PF	Typical ^b	240
2	Neoganth® MV Etch Cleaner SPS	Typical ^b	60
3	Conditioner	1.69 g/L Superfloc C-521 pH 11.5; 45 °C	240
4	Selector	29.01 g/L monoethanolamine 4.54 g/L guanidinium carbonate pH 11.5; 55 °C	300
5	Neoganth® MV Activator	Typical ^b	240
6	Neoganth® MV Reducer S	Typical ^b	180
7	Printoganth® MV Plus Electroless Copper	Typical ^b	1200

^aTap water rinse of approximately 60 s between each step.

^bOperating parameters are known to the one skilled in the art.

The following results were yielded:

- Electroless copper deposit appearance: salmon pink, blister-free
- Deposit thickness: 1 μm
- Backlight test performance: D6-D7
- 5 • Solder shock test performance: 25% ICDs following sixfold shocking (10 seconds each) at 288 °C

Due to the poor backlight and solder shock test performance, peel strength test performance was not examined.

C L A I M S

1. A method for treating a surface of a non-conductive or carbon-fibres containing substrate, the method comprising the steps
- (I) conditioning the surface of a non-conductive or carbon-fibres containing substrate,
5 the conditioning method comprising the steps of
- (a) providing said substrate;
 - (b) providing a conditioning composition comprising a nitrogen-containing compound; and
 - (c) contacting the substrate with the conditioning composition;
- 10 (II) a selector treatment of the surface of a non-conductive or carbon-fibres containing substrate, the selector treatment method comprising the steps of
- (a) providing the substrate treated according to step (I);
 - (b) providing a selector composition which
 - (i) comprises a nitrogen-containing compound, and
 - 15 (ii) has a pH of from 9 to 14; and
 - (c) contacting the substrate with the selector composition; and
- (III) activating the surface of a non-conductive or carbon-fibres containing substrate for metallization, the activation method comprising the steps of
- (a) providing the substrate treated according to step (II);
 - 20 (b) providing an aqueous, palladium-free activation composition comprising
 - (i) a first species of dissolved transition metal ions and additionally metal particles thereof,
 - (ii) one or more than one complexing agent, and
 - (iii) permanently or temporarily one or more than one reducing agent, and
 - 25 (iv) optionally one or more than one second species of dissolved metal ions being different from the first species,
- wherein
- at least of the first species, the dissolved transition metal ions and the metal particles thereof are present in a reversible equilibrium, with the proviso that

- the metal particles are formed from the dissolved transition metal ions through a continuous or semi-continuous reduction through the one or more than one reducing agent,
 - the dissolved transition metal ions are formed from the metal particles through continuous or semi-continuous oxidation of said particles, and
 - the dissolved transition metal ions and the metal particles thereof, respectively, are repeatedly involved in said reduction and said oxidation such that no precipitating agglomerates of said metal particles are formed; and
- 10 (c) contacting the substrate with said activation composition such that a transition metal or a transition metal alloy is deposited on the surface of said substrate and an activated surface for metallization is obtained.
2. The method of claim 1, wherein during and/or after step (III)(c) the majority of said metal particles is subjected to said oxidation.
- 15 3. The method of claim 1 or 2, wherein the first species is copper or cobalt, preferably copper.
4. The method of any of the aforementioned claims, wherein the metal particles of the first species in the activation composition are colloidal metal particles.
5. The method of any of the aforementioned claims, wherein the metal particles of the first species are continually or semi-continually formed *in situ* in the activation composition by said reduction after and/or during one or more than one step (III)(c) is carried out.
- 20 6. The method of any of the aforementioned claims, wherein the one or more than one reducing agent comprises a boron-containing reducing agent, preferably a borohydride.
- 25 7. The method of any of the aforementioned claims, wherein the activation composition is substantially free of or does not comprise tin ions, preferably is substantially free of or does not comprise tin ions, lead ions, germanium ions, gallium ions, antimony ions, bismuth ions, and aluminium ions, more preferably is substantially free of or does not comprise metal ions of main groups III, IV, and V of the periodic table of elements.
- 30 8. The method of any of the aforementioned claims, wherein the activation composition is substantially free of or does not comprise a compound preventing the oxidation of the metal particles and/or is substantially free of or does not comprise a stabilizer compound to stabilize the metal particles.

9. The method of any of the aforementioned claims, wherein the one or more than one reducing agent is continually or semi-continually added to the activation composition such that further metal particles are continually or semi-continually, respectively, formed from the dissolved transition metal ions of the first species, preferably added after one or more than one step (III)(c) is carried out.
10. The method of any of the aforementioned claims, wherein the dissolved transition metal ions are formed from the metal particles through oxidation by ambient air and/or oxygen gas.
11. A method for metallizing an activated surface of a non-conductive or carbon-fibres containing substrate, the method comprising the steps
- (A) providing the non-conductive or carbon-fibres containing substrate with the activated surface for metallization obtained by a method according to any of claims 1 to 10; and
- (B) metallizing the activated surface by contacting the activated surface with a first metallizing solution such that a first metallization layer is deposited on the activated surface.
12. A method for preparing an aqueous, palladium-free activation composition for activating a surface of a non-conductive or carbon-fibres containing substrate for metallization, the method comprising the steps
- (1) providing an aqueous starting solution comprising
- a first species of dissolved transition metal ions, and
 - one or more than one complexing agent, and
 - optionally one or more than one second species of dissolved metal ions being different from the first species; and
- (2) continually or semi-continually adding one or more than one reducing agent to the starting solution such that metal particles of at least the first species of dissolved transition metal ions are continually or semi-continually, respectively, formed in the solution,
- with the proviso that said metal particles are continually or semi-continually oxidized to form dissolved transition metal ions of the first species, wherein the method is used to provide the aqueous, palladium-free activation composition according to any of the claims 1 -10.
13. A selector composition which

(i) comprises

a) a first nitrogen-containing compound which is selected from ammonia, monoethanolamine, triethanolamine or mixtures thereof; and

5 b) a second nitrogen-containing compound which is selected from guanidine, guanidine compounds such as guanidinium salts, or mixtures thereof; and

(ii) has a pH of from 9 to 12.

14. The selector composition according to claim 13, wherein

10 in the selector composition the concentration of the first nitrogen-containing compound is of from 1 g/L to 50 g/L, preferred of from 2 g/L to 40 g/L, more preferred of from 3 g/L to 35 g/L, more preferred of from 5 g/L to 30 g/L, and

 in the selector composition the concentration of the second nitrogen-containing compound is of from 1 g/L to 10 g/L, preferred of from 2 g/L to 8 g/L, more preferred of from 3 g/L to 7 g/L, more preferred of from 4 g/L to 6 g/L..

15