A surface treatment process which enables a substrate (polymer) to be given specific physical properties, especially surface nanoporosity, for example with a view to electroless metallizing it, and which completely replaces surface treatment by sulfo-chromic pickling. The surface treatment includes a hybrid UV/corona treatment of the substrate surface followed by non-electrolytic metallization. A device for implementing these processes is also disclosed.
Substrate to be metalized

↓

COMBINED UV/CORONA SURFACE TREATMENT

↓

METALLIZATION BY SPRAYING

- (Wetting)
- (Sensitization)
- (Rinsing)
- Spraying of redox solutions
- (Rinsing)
  - (Thermal treatment)

↓

FINISHING LAYER

Metalized substrate

(RETREATMENT)

Recuperation of effluents
(Addition of flocculent)
(Decantation)
(Separation)

Filtrate

↓

- (Neutralization)
- Distillation
  - (Passage on activated carbon)
  - Distillate
  - Residue

Retreatment specialized center

Figure 1
PROCESS FOR OPTOPHYSICAL SURFACE TREATMENT OF POLYMER SUBSTRATES AND DEVICE FOR IMPLEMENTING THE PROCESS

TECHNICAL FIELD

[0001] The technical field of the invention is that of the surface treatment of polymer or copolymer substrates, e.g., ABS (Acrylonitrile Butadiene Styrene), in particular for covering same with metallic films.

[0002] The present invention also relates to non-electrolytic metallization methods of substrates for decoration, e.g., chrome plating of automobile parts and for aeronautics. The present invention relates to the non-electrolytic metallization of substrates for electronics, in particular the fabrication of conductive paths.

PRIOR ART

Technical Problem

[0003] In the field of non-electrolytic metallization of polymer substrates such as ABS, a pre-treatment of the substrate surface is required to facilitate the adherence of the metallic film.

[0004] The most common pre-treatment is a chemical surface oxidation treatment via sulfophoric attack, described in particular in U.S. Pat. No. 3,769,061, GB-A-1240294 and GB-A-1291351. This very corrosive treatment enables a micro- or nano-porous surface to be obtained to facilitate the mechanical anchoring of the metallic film.

[0005] The sulfophoric mixture is a mixture of sulfuric acid and potassium or sodium chromate H₂SO₄/(K₂O/Na₂O) Cr₂O₃. This mixture is very toxic and dangerous for the environment: the chromium VI salts contained in the mixture are declared by the European Union, to be category 1 and 2 human carcinogens. In addition to the toxicity problems of the compounds used, treatment surface via sulfophoric attack does not give satisfactory adherence results when the non-electrolytic metallization is carried out using the Jet Metal Technologies company’s methods, described in particular in FR-A-2,763,952 and in the French patent application filed with the number 06 10287. Indeed, because the oxidation is very deep and the metallic film very thin, the pores created by oxidation induce a phenomenon of delamination of the metallic film with time.

[0006] Other chemical oxidations are used, less commonly. It can be the use of other strong oxidizers such as potassium permanganate. The latter is flammable, noxious for humans and toxic for aquatic organisms.

[0007] It can also be an oxidation pre-treatment using ozone, by heating, described in particular in JP-A-1092377. In this treatment, oxidation is accelerated by ultra-violet (UV) irradiation. Ozone is a flammable gas which spontaneously decomposes into molecular oxygen. It is also toxic by inhalation and corrosive.

[0008] To overcome the problems linked to the use of oxidizing chemical agents which are dangerous and polluting, mechanical or physical pre-treatment solutions have been considered.

[0009] In particular, a mechanical abrasion pre-treatment via sanding which has, among other characteristics, the inconvenience of being too abrasive. Therefore, to achieve the same brilliant finish, a much thicker metallic deposition should be performed. The costs of metallization are, for this reason, considerably increased.

[0010] A physical pre-treatment is also known using plasma under reduced pressure, with heating under a controlled atmosphere. Another known physical pre-treatment of the surface is the flaming treatment.

[0011] These two types of physical pre-treatments are not very satisfactory in terms of the quality of film adherence.

OBJECTIVES

[0012] It would be desirable therefore, to have a surface treatment method which confers to the polymer substrate, specific physical properties, namely surface nanoporosity, e.g. for the non-electrolytic metallization thereof; and which would totally replace the surface treatment via sulfophoric attack.

[0013] It would be also desirable to have a non-electrolytic method for metallizing the surface of a polymer substrate, which would satisfy at least one of the following objectives:

[0014] the method should facilitate the adherence of the metallic film to the surface of the polymer substrate,

[0015] the method should make possible the deposition of as thin a metallic film as possible, having more particularly, optical properties, e.g. reflectivity and conductivity properties,

[0016] the method should be “clean”, i.e. to make the polymer surface nano-porous prior to metallization, the method should not use toxic, polluting and noxious solutions, like strong oxidizers, such as sulfophoric oxidizers or potassium permanganate,

[0017] the method should enable the effluents coming from the process to be recycled,

[0018] the method should be implemented using a compact installation which would be integrated into the current production lines, e.g. with a cabin length ranging between 1 m and 5 m, and making possible, surface treatment on automated lines.

[0019] Another objective of the invention is that of providing a device for the in-line implementation of the whole treatment and metallization method for substrates.

BRIEF DESCRIPTION OF THE INVENTION

[0020] After long investigations, the applicant found that a combined UV/Corona treatment of the surface of the, preferably polymer substrate to metalize, replaces perfectly the existing treatment by sulfophoric attack and, in addition, makes it possible to increase the adherence of the metallic film to the, preferably polymer substrate and to enhance the decorative appearance of same.

[0021] For this reason, the object of the present invention is a surface treatment method for a substrate, characterized in that the method comprises a combined UV/Corona treatment of the, preferably polymer, substrate surface.

[0022] In the sense of the invention, the term “polymer” designates the homo-polymers and the copolymers such as, e.g. Acrylonitrile Butadiene Styrene (ABS).

[0023] By “combined UV/Corona treatment”, it is understood e.g. that the substrate undergoes one or more times, a Corona electrical discharge treatment and on or more times, a UV exposure of UV treatment. These UV and Corona treatments are simultaneous or non-simultaneous, and can be performed in any order.
The corona treatment term means, e.g., that the substrate to be metalized undergoes electrical discharges e.g. of a power of 1 to 100 kilowatts 35 (kw) with a material intended to this effect and comprising one or more, preferably two or three, discharge heads (or probe). In the present invention, the term "Corona treatment" should be understood in the largest sense thereof, namely including the treatment using atmospheric plasma “air plasma”, “flame plasma”, and chemical plasma.

In the sense of the present invention, a UV treatment corresponds e.g. to the passage of the substrate to be metalized underneath an Ultra-Violet lamp, of which the emission spectrum is e.g. of 200 nm to 600 nm, with an energy peak at the wavelength of 365 nm, e.g., an Hg 125® lamp marketed by PHILIPS®.

It is preferable that the combined UV/Corona treatment of the substrate surface occurs just prior to the metallization stage, without an intermediate step. Thus, the time interval between the combined UV/Corona treatment and the metallization step is e.g. less than or equal to a few minutes. E.g., this time duration is less than or equal to 30 (thirty) minutes, preferably less than or equal to 5 (five) minutes and more preferably less than or equal to 1 (one) minute, or even a few seconds.

**DETAILED DESCRIPTION OF THE INVENTION**

**Substrate:**

In preferential implementation conditions for this above-described method, the substrate is a polymer, preferably chosen from amongst:

- Thermoplastics, advantageously from amongst the following thermoplastics:
  - polyolefins: polystyrene, copolymers of styrene such as poly(styrene-butadiene-styrene) or SBS, polypropylene, polyethylene;
  - polyamides;
  - copolymers of acrylonitrile;
  - and of methyl acrylate;
  - and of methyl methacrylate;
  - of vinyl chloride and of styrene (SAN);
  - of butadiene and of styrene (ABS), e.g. same marketed by BAYER® under the brand name NOVODUR®;
  - of butadiene, of styrene (ABS) and of polycarbonate PC;

- Thermosetting polymers advantageously from amongst the following thermosetting polymers:
  - polyimides;
  - polyesters;
  - phenolic resins;
  - epoxides.

**Combined UV/Corona Treatment:**

The combined UV/Corona treatment is chosen from amongst the following treatments: an alternation of a UV treatment and a Corona treatment, simultaneous UV and Corona treatments, a treatment comprising one or more alternation sequences and one or more sequences of simultaneous UV and Corona treatments and combinations thereof.

In the present invention, the combined UV/Corona treatment comprises at least one alternation of a UV treatment and a Corona treatment.

When the implemented substrate is made of TABS, of PABS-PC or of polypropylene, the alternation is preferably a series of UV followed by Corona.

According to a notable feature of this invention, the combined UV/Corona treatment comprises 1 to 120 times the alternation of a 0.01 second to 30 (thirty) minute UV treatment and a 0.01 second to 30 (thirty) minute Corona treatment.

Preferably, the alternation of a combined UV/Corona treatment comprises 3 to 16 alternations, namely 5 to 15 alternations and even more preferably 4 to 14 alternations; e.g. 6 or 12 alternations.

The duration of the Corona treatment during the combined Corona/UV treatment in alternation lasts preferably 0.1 seconds to 5 (five) minutes, namely 0.5 seconds to 2 (two) minutes and even more preferentially 1 (one) second to 1 (one) minute.

The duration of the UV treatment in the UV/Corona alternation lasts preferably 30 (thirty) seconds to 15 (fifteen) minutes, namely 1 (one) to 5 (five) minutes, and even more preferentially from 1 (one) to 2 (two) minutes.

In the sense of the present invention, the duration of the Corona treatment is e.g. the duration during which a unit of area of the surface to be treated is exposed or undergoes a Corona discharge using a Corona device of which the probe (or discharge head) has a given area, e.g. of 10 cm², which corresponds to the unit area to be treated. The duration of the Corona treatment can last e.g. 15 seconds for a unit area of 10 cm² of a 100 cm² flat surface to be treated. This is equivalent to a 15 (fifteen) second total Corona treatment of the surface, and to a 75 (seventy five) second combined UV/Corona treatment, corresponding to 60 (sixty) seconds of UV treatment and 15 seconds of Corona treatment.

According to the method in the invention, the alternation can start and end indifferently, either by the Corona treatment or the UV treatment during the combined Corona/UV treatment in alternation. Preferably, it is started with the UV treatment.

The object of the present invention is also a surface treatment method where the combined UV/Corona treatment as defined above is followed by a non-electrolytic metallization of the substrate treated as described.

**Metallization:**

**First Embodiment**

In a first embodiment of the metallization method as described above, the non-electrolytic metallization is a non-electrolytic metallization by the spraying of one or more redox (oxidation-reduction) solutions in the form of aerosol(s).

Metallization by spraying of one or more redox solutions in the form of aerosol(s) means that the non-electrolytic metallization step comprises at least the following steps:

- spraying of one or more redox solutions in the form of aerosol(s),
- rinsing.

In the sense of the invention, “one or more redox solutions” means e.g.:

- either a single solution containing at the same time a plurality of oxidizers and one or more reducers
or two solutions: the first solution containing one or more oxidizers and the second one or more reducers,

or a plurality of solutions, each containing either one or more oxidizers or one or more reducers, with the condition that there is at least one oxidizing solution and one reducing solution.

According to a first possibility, non-electrolytic metallization by spraying of one or more redox solutions in the form of aerosol(s) comprises, in this order, the following steps:

wetting the surface,
spraying of one or more redox solutions in the form of aerosol(s),
rinsing.

According to a second possibility, non-electrolytic metallization by spraying of one or more redox solutions in the form of aerosol(s) comprises, in this order, the following steps:
sensitizing the surface, preferably with a SnCl₂ solution,
rinsing,
spraying of one or more redox solutions in the form of aerosol(s),
rinsing.

Spraying:
The redox solution used during non-electrolytic metallization are sprayed in the form of aerosol(s) over the substrate and are preferably obtained from solutions, advantageously aqueous, of one or more oxidizing metallic cations and one or more reducing compounds. These redox solutions are preferably obtained by dilution of concentrated stock solutions. The diluent is preferably water.

It follows that according to a preferred arrangement of the invention, the spraying aerosol(s) is/are produced by the nebulizing and/or atomizing of solution(s) and/or dispersion(s) to obtain a fog of droplets smaller than 100 micrometers, preferably 60 micrometers and even more preferably 0.1 to 50 micrometers.

In the method according to the invention, the spraying of metallic solutions preferably takes place continuously and the substrate is driven into movement and undergoes spraying. E.g., when the metallic deposit is made from silver, the spraying is continuous. For a metallic deposit made e.g. from nickel, the spraying is carried out in alternation with relaxation times.

In the method of the invention, the sprayings last e.g. 0.5 to 1000 seconds, preferably from 1 (one) to 800 seconds and even more preferably 2 (two) to 600 seconds for a 1 dm² area to be metalized. The substrate can be driven into at least partial rotation during the spraying of the metallization.

According to a first method of spraying, one or more metallic cationic solutions and one or more reducing solutions are continuously and simultaneously sprayed, in one or more aerosols, over the surface to be treated. In this case, the mixture between the oxidizing solution and the reducing solution can be made just prior to the formation of the aerosol to be sprayed or by fusion between an aerosol produced from the oxidizing solution and an aerosol produced from the reducing solution, preferably prior to entering into contact with the surface of the substrate to be metalized.

According to a second spraying method, one or more metallic cationic solutions, then one or more reducing solutions are successively sprayed, by intermediary of one or more aerosols. In other terms, the spraying of the redox solution is carried out by the separate spraying of one or more solutions of one or more metallic oxidizers and one or more solutions of one or more reducers. This second possibility corresponds to an alternate spraying of the reducing solution or solutions and of the metallic salt or salts.

In the frame of the second spraying method, the association of a plurality of oxidizing metallic cations to form a multilayer of different metals or alloys is such that the different salts are, preferably, naturally sprayed separately from the reducer, but also separately one from the others, and successively. It is obvious that, in addition to the different nature of the metallic cations, using different counter-anions can be considered.

According to a variant of the spraying step, a metastable mixture of the oxidizer(s) and the reducer(s) is produced, and after having sprayed the mixture, the latter is activated, so that the transformation into metal is initiated, preferably by bringing into contact with an initiator, advantageously brought by intermediary of one or more aerosols, prior to, during or following the spraying of the reaction mixture. This variant enables the oxidizer and the reducer to pre-mix while delaying the reaction thereof until same carpet the substrate after spraying. The initiation or activation of the reaction is then obtained by any physical (temperature, UV, etc.) or chemical means.

Beyond the methodological considerations presented above and illustrated hereafter by examples, it is appropriate to give some precise information about the products implemented in the method according to the invention.

Water appears to be the most suitable solvent, without however, excluding the possibility of using organic solvents, to produce solutions from which the sprayed aerosols are going to be produced.

The redox solutions sprayed during the metallization step of the substrate are one or more solutions of a metallic oxidizer and one or more solutions of a reducer.

The concentrations of metallic salts in the oxidizing solution to be sprayed are of 0.1 g/l to 100 g/l and preferably from 1 (one) to 60 g/l, and the concentrations of metallic salts of the stock solutions are from 0.5 g/l to 10⁴ g/l, or the dilution factor of the stock solutions is from 5 to 500. Advantageously, the metallic salts are chosen from amongst the following compounds: silver nitrate, nickel sulfate, copper sulfate, tin chloride, and mixtures thereof.

The selection of reducers is preferably made from amongst the following compounds: borohydride, di-methyl-amino-borane, hydrazine, sodium hypophosphite, formaldehyde, lithium aluminum hydride, reducing sugars such as glucose and sodium erythorbate, and mixtures thereof. The selection of the reducer imposes taking into account the pH and the targeted properties of the metallization film. These routine adjustments can be done by a person skilled in the art. The concentrations of reducer in the reducing solution to be sprayed are from 0.1 g/l to 100 g/l and preferably from 1 (one) to 60 g/l, and the concentrations of reducer in the stock solutions are from 0.5 g/l to 10⁴ g/l, or the dilution factor of the stock solution is from 5 to 100.

According to a special arrangement of the invention, particles are incorporated into at least one of the redox solutions, to be sprayed at the time of metallization. The particles are thus trapped in the metallic deposit. These hard particles are e.g. diamond, ceramics, carbon nanotubes, metallic par-
articles, rare earths oxides, polytetrafluoroethylene (PTFE), graphite, metallic oxides and mixtures thereof. The incorporation of these particles into the metallic film yields special mechanical and esthetical properties to the metallic substrate.

Rinsing:

Advantageously, the rinsing step, i.e., bringing into contact the entire surface or part of the surface with one or more sources of rinsing liquid, is carried out by spraying a rinsing liquid aerosol, preferably water.

Wetting:

The wetting prior step mentioned above consists of covering the surface of the substrate with a liquid film. The choice of the wetting liquid is made from within the following group: deionized water or non-deionized water, with the possible addition of one or more anionic, cationic or neutral surfactants, an alcoholic solution comprising one or more alcohols (e.g., isopropyl alcohol, ethanol) and mixtures thereof. In particular, deionized water with an addition of an anionic surfactant and ethanol is chosen as the wetting liquid.

In a wetting variant according to which the wetting liquid is transformed into vapor which is sprayed over the substrate on which same condenses, it is preferable that the liquid is essentially aqueous for obvious reasons of industrial convenience. The duration of the wetting depends upon the area of the considered substrate and of the flow rate of the spraying of the wetting aerosol.

Sensitization:

According to a special embodiment of the invention, the sensitization step for the surface of the substrate can be implemented by means of a sensitization solution, particularly stannous chloride, e.g., according to the implementation mode described in FR-A-2 763 962. In this case, a rinsing step using a rinsing liquid such as described above, is carried out immediately following the sensitization step, without an intermediate step.

Thermal Treatment:

According to this first embodiment, the metalized substrate can undergo a thermal treatment just following the rinsing step which follows the spraying step, to reinforce adhesion.

The thermal treatment preferably takes place in an infrared oven or tunnel at a temperature from 50°C to 150°C, more preferably from 60°C to 120°C and even more preferably of about 100°C, for a duration of 5 minutes to 3 hours, preferably between 15 minutes and 90 minutes, and more preferably of about 60 minutes. The thermal treatment can also be a drying step which consists of draining the rinsing water. It can be advantageously carried out at a temperature between 20°C and 40°C, using e.g. a system of pulsed compressed air at 5 bar/pulse at a temperature of 20°C to 40°C.

All the embodiments of the non-electrolytic metallization step by spraying one or more redox solutions in the form of aerosol(s) in the sense of the invention, are more precisely described in FR-A-2 763 962 and the application for a French patent filed under the number 06 10287.

Second Embodiment

According to a second embodiment of the metallization method as described above, the non-electrolytic metallization is a non-electrolytic metallization by immersion in one or more baths containing one or more redox solutions. This method is called "chemical metallization" by a person skilled in the art.

Non-electrolytic metallization by immersion in one or more baths containing one or more redox solutions means that the non-electrolytic metallization comprises, in this order, at least the following steps:

- sensitization of the surface, preferably using a SnCl₂ solution,
- activation of the surface, preferably using a PdCl₂ solution,
- rinsing with hydrochloric acid or caustic soda,
- immersion of the substrate in one or more baths of redox solutions,
- rinsing.

Preferably, the parts to be treated are immersed in a bath mainly containing three agents: a metallic salt, a reducer and a complexing agent which prevents the spontaneous reduction and the precipitation of the bath.

All the embodiments of the non-electrolytic metallization step by immersion in one or more baths containing one or more redox solutions in the sense of the invention are more specifically described in FR 2 719 839.

According to a preferred embodiment of the method, the metallic deposit produced is a chemical nickel deposit. E.g., ATOTECH® chemical and redox solutions can be used for such a deposit:

for the activation, FUTURON® solutions can be used,

NOVIGANTH AK® solutions can be used for chemical nickel metallization.

Finishing Layer:

According to a special embodiment of the invention, the method comprises, in addition to and following the non-electrolytic metallization step, a step for producing a finishing layer.

The step of producing a finishing layer is preferably the production of an electrolytic thickening of the metalized surface. The electrolytic thickening is preferably achieved by immersing the substrate, which is at least partially metalized, in a solution bath containing electrolytes and, by passing a sufficiently high electric current between the existing electrode in the electrolytic bath and the substrate which is at least partially metalized. In the framework of the invention, the electrolytes are metallic ions suitable for being deposited onto the metalized surface of the substrate, e.g. chosen amongst the ions of the following metals: chrome, nickel, silver or copper, such as Cr²⁺, Ni²⁺, Ag⁺ and Cu²⁺. A stacking of a plurality of metallic layers produced by successive steps can occur, such as a thickening of copper followed by a layer of nickel and a final layer of chromium. The technique of electrolytic thickening is well known to a person skilled in the art. E.g., the quantity of current required to produce a 1 micrometer copper layer on a substrate having a metalized area of 1 dm² is 0.5 to 20 A from a solution of Cu⁺⁺ ions at 250 g/l. Generally, the thickness of the finishing layer produced by electrolytic thickening is from 2 to 40 micrometers. When the finishing layer is produced by electrolytic thickening, the substrate is preferably partially metalized. Partial metalization is possible namely by masking part of the surface of the substrate prior to metallization.

In the metallization method according to the invention, and preferably in the first embodiment of the metallization, the effluents coming from the different steps of the method are advantageously retreated and recycled to be used in the method, and to limit the ecological impact.
In the metallization method as described above and according to the first embodiment, the retreatment and the recycling of the effluents comprise, in this order, the following steps:  

- Recuperation of the effluents, particularly from dirty water, in a container,
- Possible addition of a flocculent,
- Possible decantation,
- Possible separation of the filtrate and sludge, namely by filtration,
- Possible neutralization of the filtrate, in particular the removal of ammonia, by addition of acid while controlling the pH,
- Distillation of the filtrate, preferably in an evaporator,
- Possible passage over a system of activated carbon,
-Reuse of the distillate, e.g. in a metallization method as rinsing water or as diluent of the redox stock solutions or disposal into the sewer.

The flocculent added to the effluents is preferably a charged organo-silicate polymer, such as same marketed by SNF FLOERGERG®.  

The separation of the supernatant and the sludge is advantageously achieved by filtration on sintered filters or by overflowing.  

The sludge can then be disposed of and directed towards a specialized centre for retreating or reusing waste.  

The obtained filtrate can be neutralized, in particular by adding an acid solution with a normality of 0.1 to 10 N until the filtrate reaches a pH of 5 to 6. The acids used for neutralizing in particular the ammonia existing in the filtrate are chosen amongst hydrochloric acid, sulfuric acid, nitric acid and mixtures thereof.

The distillation of the filtrate is preferably achieved using an evaporator, and the filtrate is heated at a temperature of 90 to 120°C. The residue which remains at the bottom of the boiler at the end of the distillation is disposed of and sent to a specialized center for retreating or reusing waste. The distilled water can be reused in the metallization method, and in particular for the dilution of stock solutions and for the rinsing and wetting steps.

The advantages of the method according to the invention are numerous. The surface treatment makes possible the control of the metallization reaction and improvement of the adherence of the metallic film to the surface. No chemical product is used for the combined UV/Corona treatment. Moreover, the effluents of the metallization, discharged by the process and which are, on an industrial scale, more than one ton per day, are retreated and reused by the process. The distilled water which comes out of the retreatment module is pure and can be used as such for the dilution of the oxidizer and reducer stock solutions, and for rinsing and wetting. This advantage is non-negligible from an economical point of view because water consumption is considerably reduced, and from an ecological point of view because the quantity of waste to be disposed of is considerably reduced. It is important to note that industrial water cannot be used by the method, and that a purification step would be required if the method would not have a module for retreating effluents and purifying dirty water. In addition, the method uses concentrated stock solutions which are diluted on-site prior to metallization. The volume of stock solutions is therefore smaller than if the solutions would be already diluted, which reduces costs, in particular for transportation.

In addition, the quantities of reducer which are used are lower than the authorized standard (ISO 14001), this compound being toxic for the environment, so reducing the quantities used is an important ecological advantage.

In addition, the electrolytic thickening which can be produced has the advantage of being selective: same only takes places on the metallized surface of the substrate, which enables embossed patterns to be created, such as conductive paths.

The object of the present application is also a method for treating surfaces including a combined UV/Corona treatment and a metallization of substrates, as defined in the above description, where a plurality of substrates are treated in line without breaking the chain. In particular, the method does not require any handling performed by man, with the exception of the steps of loading the substrate to be metallized and unloading the metallized substrate.

The method described above is advantageously implemented using a industrial metallization device which comprises the following elements:  

- At least one module for combined UV/Corona surface treatment,
- At least one module for non-electrolytic metallization.

According to a preferred embodiment of the invention, the industrial device for the implementation of the method described above comprises, in addition, the following elements:  

- At least one module for producing a finishing layer,
- At least one module for retreating and recycling effluents.

The module for combined UV/Corona surface treatment comprises one or more Corona discharge heads and one or more UV lamps. It can be, e.g. a Corona discharge tunnel marketed by the DMG® company under the name C22® and a reference UV lamp HK125® from the brand PHILIPS®.

The non-electrolytic metallization module comprises means of non-electrolytic metallization which are the current means of spraying solutions, in particular same described as in FR-A-2 763 962, or means of immersion such as electroplating lines via baths.

The means of spraying comprise, e.g. a set of HVLP (High Volume Low Pressure) spray guns, said guns being each linked to one or more pumps supplied with a solution. A first pump/gun system is provided for the wetting step. A second pump/gun system is provided for the sensitization step and a third for the rinsing. The spraying of metallic oxidizer and reducer solutions is carried out using at least two pump/gun systems: a system for the oxidizer solution, and a system for the reducer solution. For spraying the oxidizing solution, the number of guns is between 1 and 30, linked to at least one pump. The same applies to the spraying of the reducer solution which counts 1 to 30 guns. A final pump/gun system is provided for rinsing following the spraying of metallization solutions.

The means of immersion are, e.g. containers (tanks or vats) in which liquid solutions are put. The lines which are used are e.g. of the type marketed by the CORELEC® company. The non-electrolytic metallization module can also include means of thermal treatment for the metallic film, e.g.
using an IR oven or tunnel, or a system of pulsed compressed air at 5 bar/air pulsed at a temperature comprised between 20 and 40° C.

[0137] The module for producing a finishing layer comprises means of producing an electrolytic thickening of the metallized surface, particularly an electrolytic bath filled with solution containing electrolytes, at least one electrode and a device for the circulation of an electric current.

[0138] When the device according to the invention uses means of non-electrolytic metallization which are current means of spraying solutions, then the device can be, in addition, equipped with a module for retrieving and recycling effluents.

[0139] This module for retrieving and recycling effluents comprises means of recuperating effluents, which are, e.g. recuperation channels, such as chicane screens which direct the effluents towards a recuperation container, and which are intended to protect the mechanism of the conveyer on which are arranged the substrates to be metallized.

[0140] This module for retrieving and recycling effluents also comprises:

- means of decantation and separation of the filtrate and the sludge, e.g. a decanter or an overflow device,
- means of distillation, e.g. using an installation comprising one or more boilers and one or more refrigerated columns.

[0143] When the effluents are retrieved, the purified water is directed, via means of conveying liquids, e.g. pipes and pumps, towards the different modules of the method, to be reused.

[0144] According to a preferred embodiment of the device of the invention, the substrates to be metallized are placed on a means of moving the substrates from one module to another. It can be, e.g. a conveyer, particularly a belt and pin conveyer, when a metallization module is used, which comprises means of spraying. It can be, e.g. a swing tray whenever the metallization module consists of means of immersion.

[0145] Preferably, the means of moving the substrates is equipped with means of driving into rotation the substrates about the axes thereof.

[0146] The present invention also relates to a metallized substrate obtained using the method as described above, the substrate being in particular an automobile part or a part used in aeronautics.

[0147] The present invention also has as object, a metallized substrate obtained using the method as previously described, the substrate being in particular a part used in electronics such as a conductive path or a radio frequency identification (RFID) antenna.

[0148] The invention will be better understood when reading the following description of examples of implementation of the method and embodiments of the device, in reference to the appended drawings where:

[0149] FIG. 1 shows a global diagram of the embodiment of the metallization method according to the invention,
[0150] FIG. 2 shows a diagram of a device according to the invention,
[0151] FIG. 3 shows a transverse cross-section of a substrate metallized using the method according to the invention.
[0152] FIG. 4 shows a transverse cross-section of a substrate metallized using the method according to the invention.
[0153] In FIG. 4 a summary diagram of the essential and optional steps of the embodiment of the metallization method according to the invention, is shown.

[0154] FIG. 2 is a schematic representation of a device for embodying a method according to the invention.

[0155] This device comprises the following three modules:

- a combined UV/Corona treatment module 3,
- a non-electrolytic metallization module 6,
- an optional module for producing a finishing layer 16.

[0159] The combined UV/Corona treatment module 3 comprises a UV treatment cabinet 4 and a Corona treatment cabinet 5.

[0160] The non-electrolytic metallization module 6 comprises a spraying zone 7 equipped with guns 8 linked to pumps 9, each pump being linked to its own solution vat. Pump 10 is reserved for wetting the surface. Pump 11 is provided for the step of sensitizing the surface of the substrate and pump 12 for rinsing. Pumps 13 and 14 are pumps linked to redox solutions. Pump 15 is a rinsing pump.

[0161] The optional module for producing a finishing layer 16 is a cabinet for electrolytic thickening consisting of a container containing an electrolytic solution 17 and electrodes 18 and 19 in which circulates a sufficiently high current for producing electrolytic thickening. Electrode 18 plunges into the electrolytic solution bath and electrode 19 is linked to the metallized substrate.

[0162] During a process using this device, the substrate to be metallized 1 is placed on a swing tray 2 which conveys same towards the combined UV/Corona treatment module 3 where same undergoes a combined UV/Corona treatment via the UV treatment cabinet 4 and Corona treatment cabinet 5. At this stage, the swing tray 2 makes round trips between the treatment cabinets UV and Corona 5, in alternation.

[0163] The substrate which is treated is then conveyed towards the non-electrolytic metallization module 6 installed after the combined UV/Corona treatment module 3. In the spraying zone 7, pump 10 wets the surface, e.g. with water. Then pump 11 sprays a solution of stannous chloride. This sensitization is followed by a rinsing step, e.g. with water, using pump 12. Pumps 13 and 14 then spray the redox solutions required for the production of the metallic film. Pump 13 is e.g. linked to the solution of metallic ions and pump 14 is linked to the reducer solution. The actuation of these pumps can be simultaneous or consecutive. Following the metallization, a rinsing step is provided using pump 15 linked to a solution of rinsing liquid, e.g. water.

[0164] The substrate thus metallized is finally conveyed towards the optional module for producing a finishing layer 16 where the substrate undergoes electrolytic thickening. The substrate is plunged into the electrolytic solution bath, electrode 18 is plunged into the electrolytic solution bath, electrode 19 is attached to the substrate to be metallized and a current is circulated between the two electrodes.

[0165] The substrate 20 which has been metallized using the method according to the invention can then be unloaded after the production of the finishing layer.

[0166] FIGS. 3 and 4 each show a schematic transverse cross-section of a substrate metallized by an embodiment of the method of the invention.

[0167] In FIG. 3, the metallized substrate consists of three layers A, B and C. Layer A stands for the substrate, e.g. a substrate made of ABS, layer B is the metallic film, e.g. a chromium film, and layer C is the result of electrolytic thickening in a bath containing nickel sulfate.

[0168] In FIG. 4, the metallized substrate also consists of three layers called A', B' and C'. A' is a substrate, e.g. an
ABS-PC. Layer B' is a metallic layer, e.g., made of nickel, obtained via metallization with masking part of the surface. Layer C' is a copper layer, which is the result of electrolytic thickening in a bath containing copper sulfate. The deposition of this layer C' is selective and only takes place on the surface of the layer B'.

**EXAMPLES**

**Example 1**

Chromium Metallization of an ABS Substrate

A shaped part made of ABS NOVODUR® from BAYER®, on the order of 10 cm in length, 10 cm in width and 1 cm in thickness, is driven into rotation on a rotating plate at 0.5 rpm. The rotating part is then treated using an alternating UV/Corona treatment according to the following conditions:

- **0170** 1 minute under a UV HK125® (125 mW) lamp from PHILIPS® having an emission spectrum with a wavelength of 200-600 nm (peak at 365 nm).
- **0171** 1 minute Corona discharge at 32 kW with a C22® apparatus from DMG® distributed over the whole surface. The probe of the apparatus is equipped with two electrodes and a surface area of 10 cm². So every 10 cm² of the part undergoes a Corona discharge for 1.6 seconds. The probe is placed at 10 mm from the surface and the scan of the whole surface in 1 (one) minute.
- **0172** this alternation is repeated 6 times.
- **0173** The part which has been treated is placed inside a module for non-electrolytic metallization using spraying, where same successively undergoes:
  - **0174** wetting by water spraying for 5 seconds.
  - **0175** spraying of an aqueous solution of nickel salt (MSO4) with a concentration of 7 g/l simultaneously with spraying of an aqueous solution of sodium borohydride at 10 g/l for 600 seconds in alternation with relaxation times.
  - **0176** water rinsing for 10 seconds.
  - **0177** An ABS part is thus obtained, with a metallic primary layer made of electrically conductive nickel on which a finishing range is produced using electrolytic thickening according to a protocol and using a material and products known per se. This thickening consists of the following successive layers: copper (20 microns)+nickel (5 microns)+chromium (0.5 microns).
- **0178** The ABS part with a Ni metallic primary is therefore successively immersed:
  - **0179** in an electrolytic solution bath of copper ions, marketed as CUPRACIDE ULTRA® from the ATOTECH® company (current 2 A, 700 s).
  - **0180** in an electrolytic solution bath of nickel ions, marketed as NiMAC® by the company MACDERMID® (current 2 A, 150 s).
  - **0181** in an electrolytic solution bath of chromium ions marketed as the MACRO ME 8210-CROME® range by the company MACDERMID®, with a current intensity sufficiently high and a duration long enough to obtain a layer of 0.5 micrometers.

**Example 2**

Metallization with Nickel of a Part Made of ABS-PC

An ABS-PC part from BAYER®, 10 cm long by 10 cm wide and 1 cm thick, and on which part of the surface is masked in order to produce a printed circuit pattern, is driven into rotation on a rotating plate at 5 rpm. The rotating part is then treated using an alternating UV/Corona treatment according to the following conditions:

- **0183** 2 minutes under a UV HK125® (125 mW) lamp from PHILIPS® having an emission spectrum with a wavelength of 200-600 nm (peak at 365 nm).
- **0184** 1 minute Corona discharge at 32 Volts with a C22® apparatus from DMG® over the whole surface. The probe of the apparatus is equipped with two electrodes. The probe is placed at 10 mm from the surface.
- **0185** This alternation is repeated 12 times.
- **0186** The part which has been treated is placed inside a module for non-electrolytic metallization where same successively undergoes:
  - **0187** a sensitization of the surface by spraying a stannous chloride for 5 seconds.
  - **0188** rinsing the sensitization solution by water spraying for 10 seconds.
  - **0189** spraying an aqueous solution of ammonium silver nitrate of a concentration of 3 g/l simultaneously with spraying an aqueous solution of glucose at 10 g/l for 30 seconds.
  - **0190** water rinsing for 25 seconds.
- **0191** The mask is removed from a part of the surface.
- **0192** The part is thus partially metallized and immersed in an electrolytic solution bath of copper ions, marketed as CUPRACIDE ULTRA® by the company ATOTECH®. An electrode is placed in the bath and a 2 A current is applied between the electrode and the substrate. The duration of the electrolysis is 700 seconds and thickening is of 20 microns.
- **0193** A metalized and copper-thickened ABS-PC part is thus obtained.
- **0194** A standardized Peel Test ASTM B533 is run on this part. A mean value of 0.7 N/mm is obtained.

**Example 3**

Primary Metallization with Copper of a Part Made of ABS

A part of ABS of the NOVODUR® range from BAYER®, 10 cm long by 10 cm wide and 1 cm thick, and of which part of the surface is masked in order to produce a printed circuit pattern, is driven into rotation on a rotating plate at 5 rpm. The rotating part is then treated using an alternating UV/Corona treatment according to the following conditions:

- **0196** 2.5 minutes under a UV HK125® (125 mW) lamp from PHILIPS® having an emission spectrum with a wavelength of 200-600 nm (peak at 365 nm).
- **0197** 2 minute Corona discharge at 32 Volts with a C22® apparatus from DMG® over the whole surface. The probe of the apparatus is equipped with two electrodes. The probe is placed at 10 mm from the surface.
- **0198** This alternation is repeated 12 times.
- **0199** The part which has been treated is placed inside a module for non-electrolytic metallization where same successively undergoes:
  - **0200** activation using colloidal palladium of the FUTURON® range from ATOTECH® for 7 minutes.
  - **0201** water rinsing for 25 seconds.
- **0202** metallization by chemical bath of nickel of the NOVOTAN® AK® range from ATOTECH® for 15 minutes.
- **0203** rinsing in a water bath for 30 seconds.
[0204] The part which has been metalized (under a nickel layer) is immersed in an electrolytic solution bath of copper ions at 250 g/l. An electrode is placed inside the bath and a 2 A current is applied between the electrode and the substrate. The duration of the electrolysis is of 700 seconds and thickening is of 20 microns. The range is completed by an electrolytic deposit of nickel of 5 microns and a chromium layer of 0.5 microns. This copper/nickel thickening is carried out in the same way as in example 1.

[0205] A chromium-metalized ABS part is thus obtained for applications in the automobile field, in particular.

[0206] A standardized Peel Test ASTM B533 is run on the part which was obtained. A mean value of 0.75 N/mm is obtained.

1. Method for treating a substrate surface comprising a combined UV/Corona treatment of the substrate surface followed by a non-electrolytic metallization of the substrate which has been treated.

2. Method for surface treatment according to claim 1, wherein the combined UV/Corona treatment is chosen from the group consisting of an alternation of a UV treatment and a Corona treatment, a simultaneity of UV and Corona treatments, a treatment comprising one or more alternation sequences and one or more simultaneous sequences of UV and Corona treatments and combinations thereof.

3. Method for surface treatment according to claim 1, wherein the substrate is a polymer, preferably chosen amongst:

I—Thermoplastics, advantageously amongst the following thermoplastics:
  polyolefins: polystyrene, copolymers of styrene such as
  poly(styrene-butadiene-styrene) or SBS, polypropylene,
  polyethylene;
  polyamides;
  copolymers of acrylonitrile:
  and of methyl acrylate;
  and of methyl methacrylate;
  of vinyl chloride and of styrene (SAN);
  of butadiene and of styrene (ABS);
  of butadiene, of styrene (ABS) and of polycarbonate PC; or

II—Thermosetting polymers advantageously from amongst the following thermosetting polymers:
  polyimides;
  polyesters;
  phenolic resins;
  epoxides.

4. Method for surface treatment according to claim 1, wherein the combined UV/Corona treatment comprises at least one alternation of a UV treatment and a Corona treatment.

5. Method for surface treatment according to claim 1, wherein the combined UV/Corona treatment comprises 1 (one) to 120 times the alternation of a 0.01 second to 30 minute UV treatment with a 0.01 second to 30 minute Corona treatment.

6. Method for surface treatment claim 1, wherein the non-electrolytic metallization is a non-electrolytic metallization by spraying of one or more redox solutions in the form of aerosol(s).

7. Method for surface treatment according to claim 1, wherein the non-electrolytic metallization is a non-electrolytic metallization by immersion of the substrate in one or more baths of redox solutions.

8. Method for surface treatment according to claim 1, wherein the effluents are treated and recycled and wherein the retreatment and the recycling of the effluents comprise, in this order, the following steps:
  recuperation of the effluents in a container;
  distillation in an evaporator;
  use of the distillate in the method for metallization or disposal to the sewer.

9. Method for surface treatment according to claim 1, wherein a plurality of substrates are treated in line without breaking the chain.

10. Device for the implementation of the method as described in claim 1, comprising the following elements:
  at least one module for a combined UV/Corona surface treatment,
  at least one metallization module.

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