(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 May 2020 (14.05.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/094162 A1

(51) International Patent Classification:
D06M 11/83 (2006.01) *C23C 18/20* (2006.01)
C23C 18/16 (2006.01) *C25D 7/00* (2006.01)
C23C 18/18 (2006.01)

(21) International Application Number:
PCT/CZ2019/000053

(22) International Filing Date:
06 November 2019 (06.11.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PV 2018-606 06 November 2018 (06.11.2018) CZ

(71) Applicant: **BOCHEMIE A.S.** [CZ/CZ]; Lidická 326, 735 81 Bohumín, Nový Bohumín (CZ).

(72) Inventor: **VECERNIK, Josef**; Alsovice 54, 468 21 Bratrikov (CZ).

(74) Agent: **ROTT, RUZICKA & GUTTMANN A SPOL.**; South Point, Vyskocilova 1566, 140 00 Praha 4 (CZ).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title:** METHOD OF CONTINUOUS METAL PLATING OF TEXTILE MATERIAL, DEVICE TO CARRY OUT THE METHOD, METAL PLATED TEXTILE MATERIAL AND ITS USE

(57) **Abstract:** A treatment method of textile material to increase its absorption and reflectivity of electromagnetic radiation, electrical and thermal conductivity, antimicrobial characteristics wherein it is characterized in that continuously moving textile material is gradually surface treated (using chemical and also plasmatic treatment as necessary), chemically modified with a defined quantity of adsorbed nanoparticles of metals and/or their alloys, and subsequently electrochemically treated with metals and their alloys, or possibly metal oxides, and finally treated with an organic protective layer if necessary. Device to carry out the method, produced metal plated textile material and its use are also provided.

WO 2020/094162 A1

Method of continuous metal plating of textile material, device to carry out the method, metal plated textile material and its use

TECHNICAL FIELD

In recent years, textile material has been increasingly becoming the object of interest of material engineering in a wide range of industries. It has experienced significant changes in the last decade, when the interest in its innovations and applications strongly expanded in non-textile industries. Modified textile materials find application in varied fields as medicine, agriculture, machine engineering, electronics, food industry as well as in composite structures of aviation and civil engineering structures etc. Targeted modifications of physical and chemical characteristics of textile materials offer extension of applicability of knitted, woven and non-woven textile structures in the form of highly multifunctional and hybrid textiles. These are textile materials whose surface is modified in a targeted way to give the material new technically and technologically applicable characteristics as high electrical and thermal conductivity, reflectivity and absorbance of electromagnetic (EMG) radiation, antibacterial and antifungal effects etc. However, for commercial use and wide applicability of these unique textile materials, a technology is needed that would convert the experience and results of research into the application stage and to the subsequent cost-efficient mass production of modified textile material.

The present invention relates to a so far not disclosed method of continuous mass production of metal plated textile material with high electric conductivity, namely in full width, which is based on a conventional textile technology with converting operations among which operations of chemical and electrochemical metal plating are predominant. Treatment of the surface of textile material with metal is a process that always requires complex pre-treatment of the textile fiber surface to ensure subsequent precise deposition of the respective metal. From the point of view of continuous production dynamics, the present invention mainly modifies the continuous textile technology of unwinding and winding of textile material (the *roll to roll* method) in such a way to make the rates of the converting operations of textile material (plasmatic and chemical treatment, rinsing, dewatering, drying, impregnation etc.) comparable to the rates of the metal plating (chemical and electrochemical) operations.

The present invention further relates to the device for the execution of this method, metal plated textile material obtained this way and its use.

BACKGROUND ART

Based on a literature and patent search, a conclusion can be drawn that no industrially applicable continuous textile material metal plating technology based on the *roll to roll* method, namely in the full width of the textile material and in the multiple processing mode (processing of several textile material layers at the same time), with textile operations of chemical and physical pre-treatment, the entire chemical metal plating *in situ* on a horizontally moving endless band, and the final electrochemical reinforcement of the metallic layer has been disclosed in the world.

The term *roll to roll* refers to synchronous unwinding of textile material from a roll (from a coil), which is rewound onto another roll (into a coil) after passing the respective production line.

The term *full width* is a textile-industry expression for a method of processing textile material in the unfolded state, i.e. its stretching in the transversal as well as longitudinal direction. The width of the textile material is not limited, it results from the width of the production line, respectively.

A continuous technology in the sense of the present invention and in conformity to the textile-industry definition is a process characterized as synchronous, i.e. textile material moving at the same rate at all points of the production line while at the input of the production line, there is pure textile material in coils and at the end of the line, coils of metal plated and treated textile material are withdrawn for commercial purposes. From this point of view, there are documents that mention the term of continuous processing in the context of metal plating of various substrates, but in most cases, they are not associated with textile materials or in the case of textile materials they only use partial operation in an in-line arrangement (in-line metallization) and the entire process is discontinuous as disclosed in the US pat. 9,284.645. According to the authors of the patent, the continuousness is related to continuous and simultaneous spraying of two reaction solutions onto discontinuous substrates with defined toughness that are placed on a belt or chain conveyor. However, what is important is the fact that neither the graphically outlined linear arrangement of the production operations nor the

text of the patent indicate the possibility of carrying out continuous metal plating of textile material from a coil (the *roll to roll* textile material treatment principle).

Similar partial solutions can be found in the US pat. 5,076.199 and DE 41 06 696, where continuous treatment is only applicable to the transition from the "activation bath" to the chemical metal plating bath. However, the pre-treatment and subsequent operations are not synchronous. What is also important is that in both these cases, the catalytic principle of precipitation of metals is applied, which is however replaced with an original principle of electrokinetic deposition of metal nanocrystals in the present invention.

Other documents from the field of chemical and electrolytical metal plating of textile materials have the character of solving partial problems and express the current state, which is still in the experimental development stage. Although methods of chemical metal plating of non-conductive substrates have been known since the 1960's, their application for textile materials has only been intensively studied since 1976 and since the 1980's they have been industrially used for the production of textile current collectors in accumulators.

To the present, a considerable number of documents and patents have been published concerning the topic of nickel plating of textile materials for these purposes, e.g. DE 36 31 055, DE 36 37 130, DE 37 10 895, DE 39 25 232, DE 41 06 696, DE 42 16 966, DE 42 42 443, US 5,076.199.

The original methods of metal plating of non-conductive substrates, including textile materials, are based on chemical pre-treatment, mostly oxidative, with subsequent reductive activation of the materials with rare metals, mostly palladium (Pd) or silver (Ag).

The entire chemical plating with metals of the copper (Cu) and nickel (Ni) type is carried out in a catalytic manner, by immersion of activated textile material into a bath comprising a mixture of salts of the respective metals, reduction agents and additives at a certain pH value and temperature. The range of published and patented formulations of baths and operation conditions is considerable. The principle of all of them is catalytic precipitation of the respective metals on the surface of activates fibers of textile materials, no chemical reaction occurring between the bath components within the bath volume (e.g. CN101831798, US 4,925.706, US2004086646). The mentioned principle of metal plating of textile materials is characterized by a considerable induction start-up time of the entire precipitation, which is too slow for the needs of industrial production of metal plated textile material (for most commercial baths the metal plating rate achieves the value of 5 μm of the particular metal an hour). The baths can be satisfactory for piece products of smaller dimensions, but in case on

textile materials the baths deteriorate quickly and their operation is inconvenient from the economical and environmental point of view.

A certain change is represented by a principle described in the patents US pat. 9,284.645, FR97-06834 and the publication [1], which is presented by the authors as "Dynamic chemical plating", or „*JetMetal*^{TM}", consisting of injection of two reaction solutions onto a non-conductive substrate in an impulse mode in tenths of a second per pulse and a pause. For good coverage of the substrate, up to 200 pulse injections with the total time of 90 seconds need to be carried out. The reaction mixtures are aqueous solutions of metallic salts on the one hand and aqueous solutions of potassium borohydride (KBH_4; potassium borohydride) or sodium borohydride ($NaBH_4$; sodium borohydride) on the other one, and they get only mixed together on the surface of the substrate. The said borohydride reaction has been amply published and used in practice as a production process of nanocrystals in many branches. The reaction is very rapid and enables precipitation of a wide range of reducible metals in the form of nanocrystals in a solution, the nanocrystals being well adsorbed onto non-conductive surfaces under certain conditions. Surfaces treated this way are further capable of autocatalytically precipitating metals from conventional chemical metal plating baths or further preferentially adsorbing nanocrystals of the generated metal. The result is always a conductive metallic film on non-conductive substrates, which however exhibits considerably varied adhesion on substrates and physicochemical parameters. The said metal plating method has not been described in the context of metal plating of highly porous materials as is conventional textile material with the specific weight of several tens of grams per square meter.

Tests with the direct injection method with the use of the above-mentioned solutions of a borohydride and salts of metal on continuously moving textile material have exhibited non-homogeneous metal plating of textile fibers at a low (50%) metal yield (the patent US9284645 mentions the value of 60% for a solid non-textile substrate) with a considerable consumption of the expensive sodium borohydride. Electrical conductivity of metal plated textile material is substantially lower as compared to conventional metal plating and it shows a strongly crystalline character with low adhesion to the surface of textile fibers. If the said method is to be used for metal plating of textile materials, a much higher metal quantity than within a conventional metal plating method needs to be applied to obtain high electrical conductivity. Both the conventional metal plating methods based on activation with rare metals with subsequent chemical metal plating in thermodynamically stable baths, which are slow, and metal plating by injection of a metastable system of two reaction solutions with a

high reaction rate, which exhibits a strongly granular character of the metallic film, are unsuitable for continuous *roll to roll* metal plating of textile material. It is the object of the present invention to solve the said drawbacks associated with metal plating of textile materials.

DISCLOSURE OF THE INVENTION

Based on the background art, we are presenting an invention of a production method of metal plated textile material using the *roll to roll* technological process with modified continuous operations of chemical and electrochemical metal plating that solves some of the above-mentioned drawbacks. The principle of the invention is a technological process in the *roll to roll* mode with a sequence of several technological operations out of which the fundamental one is two-stage chemical reduction of metal ions, together with device to carry out these operations.

The invention is based on a method of continuous metal plating by unwinding and subsequent winding of metal plated textile material in full width, the method comprising the following steps:

under an inert gas atmosphere, or under a plastic foil barrier,
textile material is subjected to the step of

primary chemical metal plating, which consists of:

- a reaction of the aqueous solution no. 1 of inorganic salts of metallic ions comprising, according to the periodic system of chemical elements, metals of group 11 (I. B group), groups 8, 9 and 10 (group VIII. B) – light platinum metals or the iron triad or their alloys or mixtures, containing an additive comprising primary, secondary and/or tertiary amines, in an aqueous alkaline medium, at a room temperature,
- with the aqueous solution no. 2 of a reductant comprising borohydrides of alkaline metals ($M^{+}BH_4^{-}$), hypophosphites of alkaline metals ($H_2PO_2^{-}$), derivatives of formaldehyde (HCHO), or hydrazine (N_2H_4) or their mixtures, in an aqueous alkaline medium,

to activate the surface of the textile material with adsorbed metal nanoparticles or their mixtures; and

subsequently, it is subjected to the step of

secondary chemical metal plating, which consists of:

- a reaction of the aqueous solution no. 3 of inorganic salts of metallic ions comprising, according to the periodic system of chemical elements, metals of group 11 (I. B group), or the iron triad or their alloys or mixtures, containing an additive comprising primary, secondary and/or tertiary amines in an aqueous alkaline medium,
- with the aqueous solution no. 4 of a reductant comprising borohydrides of alkaline metals ($M^+BH_4^-$), hypophosphites of alkaline metals ($H_2PO_2^-$), derivatives of formaldehyde (HCHO), hydrazine (N_2H_4) or hydroxylamine (NH_2OH), their mixtures, in an aqueous alkaline medium,

to fill the 3D structure of the textile material with metals or their alloys.

The first (primary) stage of the chemical metal plating according to the present invention is based on a non-catalytic reaction of metallic ions with reducing agents producing metallic nanoparticles that are deposited on non-conductive substrates, particularly textile materials, in an electrokinetic and diffusion manner. Adsorption of the nanoparticles of metals and their alloys on fibers of the textile material provides a metallic film with a nanometric thickness that activates the textile material for the subsequent (secondary) chemical metal plating. Nanoparticles of metals and their alloys generated by common chemical processes are characterized with their electric charge, quantified as the zeta potential, the value and potential of which generally depend on pH of the medium, the contents and character of the present ionic and non-ionic substances, the temperature and size of the nanoparticles.

Textile fibers in aqueous media are also characterized with the zeta potential the value and polarity of which also depends on pH of the medium, the contents and character of the present ionic and non-ionic substances, on the temperature and last, but no least, also the state and type of material. Adsorption of nanoparticles onto textile fibers then depends on many parameters influencing mutual electrostatic tension between the nanoparticles of metals and their alloys and fibers of the textile material the character and direction of which is induced by the polarity of the zeta potentials of the nanoparticles and textile fibers. The selection of the physicochemical conditions of the technological process according to the present invention is used to adjust the electrostatic tension between the zeta potentials of the nanoparticles and textile fibers in such a way that the nanoparticles of metals and their alloys are very quickly

attracted and adsorbed on the textile fibers. The adsorption rate under these conditions, expressed in grams of deposited metal per m^2 per a time unit then depends on the concentration of nanoparticles in the reaction mixture, more accurately expressed, on the reaction rate of occurrence of these nanoparticles. What must also be ensured for a successful course of deposition of metals or their alloys on textile fibers is that the instantaneous rate of occurrence of nanoparticles through a redox reaction of metal ions with reduction agents should be comparable to the rate of their immediate adsorption so that their equilibrium concentration should not exceed the critical value when undesired coagulation of nanoparticles starts to appear. The kinetics of the entire process of deposition of metals or their alloys according to the present invention is optimized on the basis of a kinetic measurement of the time dependence of the zeta potential of nanoparticles of metals occurring during the primary reaction. Data obtained by the measurement depending on the composition of the reaction solution represent the basis for the formulation of the final composition of the primary solutions. The objective of optimization of the kinetics of the deposition process of metals or their alloys is mainly to adjust compatibility with the technological speed of the line, defined as the speed of movement of the textile material in full width in meters per minute.

The technological process according to the present invention then consists in a determined optimum setting of all the above-mentioned parameters to make the rate of the primary metal plating reaction, expressed as time in minutes that is necessary for at least 80% deposition of metals or their alloys, correspond to the speed of movement of the textile material in full width and the length of the endless conveyor of the primary part of the line.

The above-mentioned principle of optimization of the technological process according to the present invention is used both within the primary, and the secondary chemical metal plating of textile material.

The primary metal plating refers to activation of the surface of fibers of the textile material with adsorbed particles of metals and their alloys, an important precondition for successful activation being the smallest possible size of adsorbed metal particles, their adequate concentration and homogeneity on the fiber surface (the “film character”). This precondition can be met according to the present invention by means of a non-catalyzed kinetically controlled redox reaction of suitable complexes of metal ions with reducing substances at suitable selected concentrations of the constituents, pH and temperature.

To achieve the best possible conditions for the adsorption of metal nanocrystals on textile fibers, according to the present invention, anions with the capability of forming

complexes with ions of these metals must be excluded from the formulation of the solutions for the primary chemical metal plating (a negative influence on the zeta potential of the nanoparticles).

An equally important precondition for successful (quantitative) adsorption of nanoparticles is the shortest possible path of their diffusion from the solution onto the fibers. The said precondition is best met by the methodology of precipitation of nanoparticles directly in the 3D structure of the textile in the "in situ" mode in cooperation with forced movement of the reaction solutions within this structure.

Another precondition for successful adsorption of nanoparticles on textile fibers with substantial elimination of their coagulation consists in ensuring the least possible volume of the reaction solution outside the 3D structure of the textile.

In practice, these preconditions are, according to the present invention, achieved by separate (simultaneous) application of two reaction solutions onto the moving textile material in full width, which is placed on a synchronously moving, horizontally situated endless belt. The optimum quantity of the applied reaction solutions, their ratios and concentrations are adjusted with respect to the type, specific weight and thickness of the processed textile material in such a way to only completely fill the 3D structure of the textile with the mixture of the reaction solutions whose volume and concentration of the constituents per m^2 of textile will be sufficient to achieve the required activation of the textile material.

Under the said conditions, fine metal nanoparticles (on the order of single nm) are deposited, producing a highly homogeneous film of the particular metal or alloy. Coagulation of the metal nanoparticles (to the particle size of tens of microns) producing an undesired crystalline film is strongly suppressed under these conditions. Metal nanoparticles in the solutions are quickly oxidized by the atmospheric oxygen and to eliminate its influence within the line, an inert atmosphere or a barrier principle is used in the form of an auxiliary endless plastic belt applied horizontally on the textile material in full width at the same movement speed.

A universal reducing substance is an alkaline borohydride, especially sodium borohydride ($NaBH_4$), as its use in other industries has considerably reduced its commercial price and at present, it is already produced industrially. A certain problem is represented by its quick hydrolysis at lower pH values of the solution and emissions of hydrogen. Metal nanoparticles generated by sodium borohydride are always alloys of the metal with elementary boron (1-10% by weight), depending on pH and temperature. Other usable

reduction agents are alkaline hypophosphites ($H_2PO_2^-$), derivatives of formaldehyde (HCHO) and hydrazine (N_2H_4), which can be advantageously used for the deposition of alloys.

The second (secondary) stage of chemical metal plating according to the present invention is based on a modification of generally known catalytic (autocatalytic) processes of stable reaction solutions of complexes of metals with reduction agents that occur on the surface of primarily metal plated (activated) fibers of textile material. On absorbed nanoparticles of a metal, for instance nickel, oxidation of the hypophosphite is strongly catalyzed on the Ni surface while electrons are released that are employed within delocalization on the nickel surface to reduce metal ions (Ni, Cu). Similarly, on a copper surface, copper ions are autocatalytically reduced with the use of reduction agents of the borohydride (BH_4^-), formaldehyde (HCHO), hydroxylamine (NH_2OH) and others. Reactions proceeding in cooperation with the surface on which metal is deposited exhibit a provably higher metal plating quality than metal plating by means of nanoparticle deposition.

On the other hand, these generally known chemical metal plating processes are based on thermodynamically stable baths that are kinetically slow at a normal temperature, and thus unsuitable for use within the *roll to roll* process according to the present invention.

It was necessary to experimentally find such thermodynamic conditions for the said catalytic reactions on the primary metal plating surface to proceed at a normal temperature at a sufficient rate, in our case on the order of several minutes, while the rates of uncatalyzed reactions within the reaction mixture volume must be negligible.

The technological process of the secondary metal plating according to the present invention consists in formulation of two reaction solutions that are applied on textile material in full width placed on an endless conveyor in the form of a reaction mixture prepared before the application or in the course of the application at such a rate for the 3D structure of the textile material to be completely filled. The optimum composition of the solutions, pH and concentrations of constituents depend on the character of the textile material, but in any case they must ensure the technologically required metal plating within the time period given by the line in the *roll to roll* mode. The secondary metal plating according to this invention makes it possible to apply pure metals as Ni, Co, Cu and Ag or their unlimited mixtures with the use of a borohydride (sodium ($NaBH_4$), potassium (KBH_4) and lithium salt ($LiBH_4$)) alone or its mixture with sodium hypophosphite (NaH_2PO_2). The metallic coatings always comprise a certain percentage of boron or boron with phosphorus.

The process of primary and secondary chemical metal plating according to the present invention proceeds at a defined rate immediately after mixing of the reaction solutions or after

the contact with the primary metal plating in the 3D structure of the textile material (*in situ* process).

The application of reaction mixtures on continuously moving textile material can be implemented by continuous single-point or multiple injection under a reverse movement of the nozzles, simultaneous pouring, spreading, with or without a lamella blade, or with a roller, or by "slot die" coating while the application of the solutions must ensure 100% and even filling of the pores of the textile material in full width.

The chemical metal plating provides a sufficiently conductive film on the surface of the fibers that can be subsequently reinforced with the same or different metal or alloys with the possibility of surface finish with protective varnishes.

The device for the implementation of the above-mentioned textile material metal plating technology is designed and structurally conceived in such a way to achieve the highest possible production capacity, all the technological conditions being met. The speed of the technology according to the present invention is limited by the reaction rates of chemical metal plating, which cannot be accelerated without a decrease of the metal plating quality and which proceeds on the order of several minutes from the application of the reaction solutions until the end of the reaction. Therefore, the design of the optimum continuous operation process in the *roll to roll* arrangement has been adapted for an up to five times increased capacity, the given rate of the production device in the range of 0.5 to 2.0 meters in a minute being maintained.

With the selection of a suitable textile material (material with high porousness) and adaptation of the design of the production device, the production capacity can even be increased more than five times, the given rate and size of the line being maintained.

The unwinding operation according to the present invention enables synchronous central unwinding of up to five coils with full width at a rate of 0.5 to 2.0 m/min, the unwound textile being vertically layered into one belt (grouping). With a suitable modification of the production device, e.g. extension of its length, the rate can even be further increased. The winding operation of finished products enables synchronous central winding onto up to five (or more) separated coils in full width at a rate of 0.5 to 2.0 m/min.

All the technological processes proceed continuously on the horizontal level between the unwinding and winding operations the rates of which are controlled and monitored by the central control unit.

The technological operations of chemical metal plating according to this invention are implemented on horizontally situated endless conveyor belts 8, 8′ made of plastic (e.g. PVC,

PE, PP, PET) the movement rates of which are the same as the movement rates of the textile material to be metal plated.

During long-term operation, these belts also get metal plated and the undesired plating must be continuously removed. A removing device 9 at the bottom side of the belt is used for this purpose that applies an aqueous solution of an acid (e.g. nitric acid) onto the belt, then rinses the belt with washing liquid and wipes off the excessive liquid.

Between individual technological operations of the present invention, cleaning stations are located that are based on a sequence of vacuum suction of residues of the process liquid, rinsing with demineralized water and suction of excessive water from the treated textile material. Waste from the cleaning stations is drained into storage tanks where residues of heavy metals are converted to poorly soluble precipitates and subsequently processed in the central cleaning station. All the reaction solutions are stirred centrally and transported to the production device via a pipeline.

DETAILED DESCRIPTION OF THE INVENTION

Textile material

The selection of the textile material has been driven by the effort to achieve high universality for the use in widest possible fields of clothing constructs, design, electrical engineering, package industry, civil engineering etc. At the same time, this selection made it necessary to specify requirements for the parameters of the continuous mode of the production device. With respect to these reasons, a decision was made to implement the metal plating process, or to construct the production device for textile material with high porousness, mechanical strength in all the directions, low specific weight (up to 100 g/m^2, preferably up to 60 g/m^2) in the form of woven or non-woven textile or fibers.

The textile material can be a natural or synthetic fabric of the organic or inorganic origin or their mixture. From the point of view of chemical composition, these may be natural (e.g. cotton, wool, silk, viscose, cellulose in general), synthetic (e.g. polyester, polypropylene, polyamide, polyethylene terephthalate, polyethylene, polyacrylate, polyurethane, polystyrene, glass) or combined textile materials (e.g. cotton/polyester, wool/polyester, nylon/cotton, wool/polyamide). A suitable representative of these materials is e.g. a polyester composite non-woven textile Milife made by JX Nippon ANCI Corporation with the specific weight of 10 or 30 g/m^2 and the tensile strength of 25N/50 mm for MD and 18N/50 mm CD.

Textile material represents a variable group of substances the surface characteristic of which strongly depend on the history/method of its production. The principal parameter for metal plating is good wetting of textile fibers in the reaction mixtures of chemical metal plating. Wettability of textile materials, or their high surface tension can be achieved through their suitable treatment (physical, chemical or biological or a combination of methods); however, low time demands represent a precondition for implementation of such treatment within the line according to the present invention. A treatment of textile materials, e.g. with permanent hydrophobization, is very complicated and time-consuming and it must carried out separately before the metal plating.

Description of the design and technology

Fig. 1 presents a schematic description of the structural and technological arrangement of a *roll to roll* line for metal plating of textile material according to the present invention, which graphically specifies the sequence of consecutive six synchronously proceeding technological operations.

1. Textile material unwinding and grouping

Textile material in the form of a coil having a defined width is centrally unwound and vertically grouped into a textile material belt consisting of up to five layers of the textile material while the sum of specific weights of individual layers should not exceed 100 g/m^2. The unwinding rate and tension in individual layers are controlled centrally in such a way to be constant, i.e. synchronous in all the parts of the line. The unwinding rate is determined by the movement speed of the grouped textile material, its tension being adjusted by the winding and drive units within the line (conveyor belt drives).

2. Textile material treatment

The second part of the continuous line according to the present invention represents a process(es) and suitably designed associated devices wherein the textile material is treated physically or by the action of chemical agents to achieve high wettability in aqueous solutions and to increase adhesion of the metal to the fiber by modifying the fiber surface trough a change of its structure or chemical composition.

Naturally hydrophilic textile materials (e.g. cotton, viscose) or materials that are easily subject to hydrolysis by the action of alkaline hydroxides at an elevated temperature or modification by suitable chemical agents (by their adsorption on the surface or surface

reaction with surface functional groups of the textile material) do not need to be physically, in this case plasmatically, treated (e.g. polyester, polyamide).

On the other hand, textile materials that are naturally strongly hydrophobic and non-reactive (e.g. polyethylene, polypropylene) require the use of plasma in any case.

2a. Physical treatment of textile material

Physical treatment of textile material refers to its exposure to the effects of a plasma discharge in the device 2a, the necessity and objectives of execution of the plasma treatment being dependent on the type of textile material [2]. Plasmatic treatment of textile material in full width is carried out by its continuous passage through a plasma discharge, which is implemented under atmospheric conditions by means of either a barrier discharge, or high-frequency corona. In both the cases, high frequency discharges are employed between two electrodes separated by at least one dielectric with inserted high voltage of up to 80 kV at a frequency of up to 20 kHz, and a power of 400 to 2000 W. The time period of exposure to plasma is determined by the movement speed of the textile material and the width of the electrodes and varies on the order of a few seconds. If the plasma generator is suitably adjusted, the surface of textile fibers is strongly eroded by the effects of plasma due to impacts of accelerated electrons and gas ions. At the same time, impurities are also removed from the surface. After plasma treatment, the fiber surface generally exhibits high surface energy (50–60 mN/m), which however rather pertains to a thin low-molecular oxidized layer that is not well attached to the fiber surface. The presence of the said low-molecular oxidized layer then has a very negative effect on adsorption and adhesion of metal nanoparticles and reduces homogeneity of the final metal plating of textile materials.

2b. Chemical treatment of textile material

If the textile material has been subjected to plasma treatment, during continuous movement, the textile material treated by plasma must be subjected to effects of a cleaning bath to remove the low-molecular oxidized layer from the fiber surface, to expose the eroded surface of the fibers, and to adjust concentrations of active groups (-OH, -HCO, -COOH, -NH_2 etc.) on them.

If the textile material has not been subject to plasma treatment, under continuous movement, the textile material is exposed to the effect of chemical agents that do not have the character of surfactants and that are suitably absorbed or superficially react with functional groups (e.g. -OH, -HCO, -COOH, -NH_2) on the textile material surface. All these treatments

lead to such an increase of subsequent adsorption and adhesion of the respective metal on textile material fibers that would not be possible without their execution. The operation parameters of the cleaning bath are adjusted by the selection of solutions, pH and temperature in such a way that the treatment of the textile material should be as efficient as possible within the shortest possible time, on the order of a few minutes, i.e. from 0.5 to 2 minutes. The composition of the cleaning bath depends on the type of the textile material, but in general, an alkaline bath with pH in the range of 10 to 14 at the temperatures of 60 to 80 °C is employed. The alkaline bath is formulated from aqueous solutions of hydroxides of alkaline metals (NaOH, KOH and LiOH) in the concentration range of 1 to 20% by weight. Depending on the type of the textile material, the bath may also comprise additions of oxidizing substances as e.g. hydrogen peroxide (H_2O_2) or peroxides of inorganic acids (e.g. peracetic acid (CH_3COOOH), or their salts (sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$) and sodium perborate ($NaBO_2 \cdot H_2O_2 \cdot 3H_2O$)). Depending on the type of the textile material, for hydrolytic treatment, the above-mentioned alkaline bath can be used, having suitable pH and containing inorganic substances as alkaline silicates, carbonates, phosphates and others.

Unlike many metal plating processes known in the world, the use of surfactants must be principally avoided according to the present invention, both within the treatment process and in the metal-plating stages.

The station is structurally designed as a pool bath with vertical immersion and emersion with a subsequent three-roller assembly for pressure removal of excessive solution from the bath by rinsing with demineralized water (distilled water can possibly be used) and vacuum removal of excessive water from the textile material belt.

3. Primary chemical metal plating of textile material

The design of the part of the line – unit 3 for primary chemical metal plating of textile material in full width under continuous movement according to the present invention is based on using a horizontally situated endless conveyor belt 8 to transport the textile material, to place the textile material in a horizontal position and at the same time to carry a mixture of the reaction solutions no. 1 and no. 2 of the primary chemical metal plating. The conveyor with a driving and tensioning assembly of rollers, with a horizontal sliding and flat liner is fitted with a commercial belt or belt made of non-woven foil the width of which is 10 cm bigger than that of the textile material. The surface of the belt can be made of PVC, PU, PE, PP, PET etc., the most suitable being PVC. The length of the belt is set in such a way that at the given length and movement speed of the belt in the range or 0.5 to 2 meters in a minute,

80% deposition of the metal on the textile material should be accomplished. The usual setting of the conveyor length is 1.5 to 3 meters. The movement speed of the conveyor belt is the same (synchronous) as the speed of the textile material. The primary part of the line further comprises an application device 10, deactivation device 9, belt device 11 to eliminate the influence of atmospheric oxygen in the form of an endless belt and a terminal device 12 to clean the chemically metal plated textile material. According to this invention, the application device 10, which is situated at the beginning of the conveyor belt 8, must enable simultaneous application of two reaction solutions of primary chemical metal plating under the designations no. 1 and no. 2. The mutual ratio of the applied solutions can be adjusted and maintained at a constant ratio while they only get mixed in the 3D structure of the textile material (*in situ* process). Continuous application of the solutions no. 1 and 2 can be realized with the use of generally known operations as e.g. injection with linear transversal movement of the nozzles, dual pouring with longitudinal spreading with a blade or roller or the *slot die* application. The control of the application rate of the solutions in ml/minute must ensure reproducible and 100% filling of the 3D structure of the continuously moving textile material.

An important part of the conveyor belt is a deactivation device 9 that is situated at the bottom part of the conveyor belt 8.

During the continuous operation of the line, the surface of the conveyor belt 8 also gets activated and metal plated and this metal plating must be continuously removed. The removal of undesired metal plating from the conveyor belt 8 is achieved through its dissolution with diluted nitric acid (e.g. 10% by weight solution) with a subsequent rinse with demineralized water by means of the deactivation device 9 and mechanical wiping. The process of primary metal plating is inhibited by atmospheric oxygen and its influence can be eliminated with a belt device 11 to eliminate the influence of atmospheric oxygen in the form of inert atmosphere, or with a barrier made of plastic foil in the form of an endless belt, which however must also be reproducibly cleaned to remove undesired metal plating, namely with diluted nitric acid. The station of primary metal plating is terminated with a considerate rinse of the activated textile material in the terminal device 12 with demineralized water with vacuum suction of excessive water.

The textile material primarily treated this way then continuously passes into the station of secondary chemical metal plating. From the technological point of view, the primary chemical metal plating process is a redox process between complex metal ions contained in the solution no. 1 as oxidizing agents and substances of a reduction character contained in the solution no. 2, whose mutual ratio, concentration, ambient pH and temperature are adjusted in

such way for the reaction between them to be accomplished within the time period during which the conveyor belt covers the technological length of 1.5 to 3 meters.

For the primary chemical metal plating process according to the present invention, metal ions of copper (Cu), nickel (Ni), cobalt (Co), silver (Ag) or palladium (Pd) can be used. With respect to the price of silver and palladium, their use is not preferred. Preferably, ions of copper and nickel as such or in a mixture are used.

For the preparation of the solutions, they are used in the form of inorganic salts with anions that do not have the ability to work as ligands in complexes (sulfates, nitrates and perchlorates) out of which sulfates are mostly used.

The rate of the reaction between the metal ions and reducing substances can be controlled with additives based on substances forming complex compounds with these ions. The said general rule is applicable in our case, but according to the present invention it is only restricted to substances having a non-ionic character. For these purposes, primary, secondary and tertiary amines or their mixtures that are well soluble in water even at high pH can be preferably used, as e.g. ammonia (NH_3), ethanolamine ($NH_2C_2H_4OH$), diethanolamine ($(C_2H_4OH)_2NH$), triethanolamine ($(C_2H_4OH)_3NO$), propanolamine ($CH_3CH(OH)CH_2NH_2$), methylethanolamine ($CH_3NHC_2H_4OH$), dimethylethanolamine ($(CH_3)_2NC_2H_4OH$)), diethanolmethylamine ($CH_3N(C_2H_4OH)_2$).

The solution no. 1 for the primary chemical metal plating is adjusted with sodium hydroxide (NaOH) to pH in the range of 8 to 10, preferably to 8.5 at a set temperature from 20 to 25 °C.

The mutual ratio of the metal ion and amine in the solution no. 1 for primary chemical metal plating is set in the range of 1:1 to 1:8, the preferred ratio is 1:4 to 1:6.

The solution no. 2 for the primary chemical metal plating is an aqueous solution of a reducing agent in the form of sodium borohydride ($NaBH_4$) as such or in mixtures with sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$).

pH is adjusted with sodium hydroxide to the value of 12 to 14.

According to the present invention, the solutions no. 1 and no. 2 of the primary chemical metal plating can be applied onto the textile material in mutual volume ratios of 10:1 to 1:10 while the ratios of 2:1 to 1:2 are mostly preferred, the 1:1 ratio being advantageously used.

If the conditions are selected optimally, after the primary chemical metal plating process, the surface of fibers of the textile material is covered by nanocrystals of the used metals and their amorphous alloys with boron and partly phosphorus in the form of a

continuous film with a very high surface resistance (some MΩ to tens of MΩ per square; within this invention, the term square refers to a delimited area of textile material in full width, with the dimensions of 5x5 cm, while the dimensions of the sides of the delimited area are not restricted in any way, or they result from the sensitivity and accuracy of the used measurement device of surface resistance, respectively), which represents the basis for the catalytic and autocatalytic processes of the secondary chemical metal plating in the next stage. The design of the primary part of the chemical metal plating is terminated by a rinse of the textile material with demineralized water and suction of its excess.

4. Secondary chemical metal plating of textile material

A part of the line device – unit 4 intended for the secondary chemical metal plating of textile material in full width during continuous movement is structurally designed in the same way as the station for the primary chemical metal plating according to the present invention. It is based on a conveyor belt 8′, preferably made of PVC, that comprises the same application device 10 of the solutions of the secondary chemical metal plating no. 3 and no. 4, the same deactivation device 9 for continuous cleaning of the conveyor belt 8′ to remove undesired metal plating, a belt device 11′ to eliminate atmospheric oxygen and a terminal device 12 to remove residues of the chemical metal plating solutions. The length of the conveyor belt 8′ varies in the range of 2 to 6 meters depending on the selected metal plating technology.

From the technological point of view, the secondary chemical metal plating process according to the present invention is again a redox process between complex metal ions as oxidizers and substances of a reducing character whose mutual ratio, concentration, ambient pH and the temperature are adjusted in such a way for the reaction to be accomplished within the 3D structure of the textile and within the time period that is determined by the movement speed of the conveyor belt and its length (2 to 6 meters).

A substantial change in the secondary metal plating process as compared to the primary metal plating is a change of the reaction mechanism from the process of thermodynamically unstable reduction of metallic ions in the entire volume of the reaction solution to catalytic and autocatalytic processes, mostly restricted to the resulting primary metal plating surface.

The secondary metal plating solution, produced by mixing of the reaction mixtures referred to as no. 3 and 4 together, is relatively stable at a normal temperature, but on contact with the primary metal plating layer a quick catalytic or autocatalytic reaction occurs that is associated with precipitation of metal on the primary metal plating surface.

For the process of the secondary chemical metal plating according to the present invention, metal ions of copper (Cu), cobalt (Co), silver (Ag), nickel (Ni) or their mixtures can be used again, namely in the form of their sulfate and hypophosphite salts, which are converted to mixed complexes of non-ionic amines in the secondary chemical metal plating solution no. 3. For these purposes, primary, secondary and tertiary amines or their mixtures can be used again, e.g. ammonia (NH_3), ethanolamine ($NH_2C_2H_4OH$), diethanolamine ($(C_2H_4OH)_2NH$), triethanolamine ($(C_2H_4\ OH)_3NO$), propanolamine ($CH_3CH(OH)CH_2NH_2$), methylethanolamine ($CH_3NHC_2H_4OH$), dimethylethanolamine ($(CH_3)_2NC_2H_4OH$)), diethanolmethylamine ($CH_3\ N(C_2H_4OH)_2$).

pH values of the solutions no. 3 are adjusted in the range of 9 to 11, preferably to 9.5 to 10 at a set temperature of 20 to 40 °C.

The mutual ratio of the metal ion and amine in the solution no. 3 is set in the range of 1:1 to 1:4, the preferred ratio is 1:2 to 1:3.

The secondary chemical metal plating solution no. 4 is an aqueous solution of the reducing agent sodium borohydride ($NaBH_4$) with possible additions of sodium hypophosphite the pH of which is adjusted to pH 12 to 14 with sodium hydroxide.

The concentrations of the secondary chemical metal plating solutions are 10 to 20 times higher than the concentrations of the primary chemical metal plating solutions. The mutual volume ratio of the secondary chemical metal plating solutions during application is preferably in the range of 1:2 to 2:1 while their total volume per a time unit must at least correspond to the free volume in the 3D structure of the textile material to be metal plated during the said time unit.

The final product of the secondary chemical metal plating station is electrically conductive textile material with the area resistance of 10 to 100 Ω per square, which is cleaned by vacuum suction of residues of the secondary chemical metal plating solutions, rinsing with demineralized water and vacuum suction of excessive water.

The clean metal plated textile material continuously passes to the electroplating station at the rate of 0.5 to 2.0 meters in a minute.

5. Electroplating of textile material

The design of the line part – device 5 for electroplating of textile material in full width under continuous movement according to the present invention is based on the conventional electroplating technology of the pool type with external filtration, a basket anode with

replenishment of the anode metal and a cathode, which is the chemically metal plated textile material.

The anode metal can be Au, Ag, Ni, Co, Cu, Sn, Zn, In, Bi, Cr and their alloys while electroplating baths are solutions of the respective metal salts, mostly in the sulfate or chloride form (e.g. copper sulfate ($CuSO_4 \cdot 5H_2O$), tin sulfate ($SnSO_4$), zinc sulfate or chloride ($ZnSO_4$ or $ZnCl_2$), nickel chloride ($NiCl_2$)).

Strongly acidic baths based on sulfuric or hydrochloric acid are preferred.

The bath can comprise gloss-making, wetting or other additives modifying the resulting electroplating of the textile material, which must exhibit the required electrical, magnetic and mechanical properties. For this purpose, the entire electroplating process is continuously monitored and adjusted as necessary to reproducibly achieve these characteristics. The compositions of electroplating baths and precipitation conditions as the cathodic and anodic current density and inserted voltage are generally known and have been widely published in the world [5–7].

The electroplated textile material is also cleaned by vacuum suction of the residues of the solution from the electroplating baths, rinsing with demineralized water and vacuum suction of excessive water.

6. Varnishing of the metal plated textile

According to the present invention, the metal plated textile can be already protected from atmospheric and chemical corrosion through the selection of corrosion-resistant alloys, e.g. copper-nickel (also referred to as white copper) in the chemical metal plating or electroplating stages.

Corrosion resistant-metals and alloys are suitable, but in most cases their entire metallic surface exhibits a high friction coefficient value and subsequently, such materials easily abrade against each other. In the case of textile material, this is a substantial defect. One possibility of increasing the corrosion and abrasion resistance of metal plated surface consists in fitting the surface with a protective layer with high adhesion to the metallic surface even under wet conditions (hydrophobic properties) and with a low friction coefficient.

Using the process according to the present invention, the metal plated textile can be fitted with a protective layer in a varnishing device 6 by varnishing under continuous movement by immersion into a bath with commercially available water-dilutable dispersion and emulsion varnishes and glazing, mostly based on highly hydrophobic fluorocarbon polymers of type C8 or C6 or lubricants on the basis of sodium alkyl thiolates, or formulated

with the presence of nanoparticles (nanotechnology) [8]. The varnishing or application of lubricants require processes that will not cause a considerable reduction of permeability of the textile material (according to EN ISO 9237) and will not change its sensual characteristics and especially will not cause sticking of the grouped textile belt together.

The said characteristics and conditions during continuous wetting of textile material in full width can be achieved using the process according to the present invention, which is characterized by adjusting the viscosity and concentration of varnishes or lubricants to such a value that the subsequent pressure treatment on rollers, vacuum suction of excessive varnish or lubricant, overpressure separation of individual textile layers with hot air and final hot air drying at temperatures of 80 to 200 °C for several minutes should only reduce the air permeability by 10% at the most. If the said technological operations do not cause sticking of the grouped textile belt together and the 10% limit or permeability reduction is met, good sensual feeling of the textile and high-quality protective function of the varnish or lubricant can be expected.

7. Winding of metal plated textile material

The final product in the form of metal plated, varnished and dry textile material in full width is continuously divided into individual centrally controlled coils in the ungrouping device 7 according to this invention. The winding rate and tension is synchronized with the unwinding and line processes through the central control unit. The winding device 7 comprises a structural and program solution of the need to change the tension in the textile belts on transition from the technological part to the winding part. Winding sometimes requires a different tension due to tightening of the wound textile on the beam.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 – A schematic description of the structural and technological arrangement of the continuous *roll to roll* line;

Fig. 2 – Dependence of attenuation of electromagnetic radiation on its frequency.

EXAMPLES

Operating parameters of the continuous line according to the present invention used for Examples no. 1 to 7.

The input textile material is non-woven polyester textile with the width of 1.1 m and specific weight of 30 g/m^2. The unwinding and winding rate and travel speed of the textile material is 1 meter in a minute. The number of layers of the textile material to be metal plated is one layer. The chemical treatment is carried out in a bath with the composition of 100 g of sodium hydroxide (NaOH) and 10 g of sodium percarbonate ($Na_2CO_3 \cdot 1{,}5H_2O_2$) per 1000 ml of demineralized water (DW) at the temperature of 60 °C for 1 minute. The primary chemical metal plating proceeds in the range of 2 minutes (the length of the conveyor belt is 2 meters) in a protective atmosphere of nitrogen. The secondary chemical metal plating proceeds in the range of 5 minutes (the length of the conveyor belt is 5 meters). The continuous electroplating proceeds in a constant current electroplating (galvanostatic) mode for 1 minute. Further, continuous wetting is carried out in the Pragokor Seal Cu protective varnish, then overpressure dewatering and hot-air drying at 120°C for 2 minutes.

Example no. 1

Primary chemical metal plating:

Solution no. 1: 3 g of $CuSO_4 \cdot 5H_2O$, 3 g of $NiSO_4 \cdot 6H_2O$, 14 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 25 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Electroplating: Copper plating bath Pragogal 2500, Pragochema a.s. Praha, Cu anode.

Characteristics: Specific surface resistance 0.1–0.3 Ω/square.

Example no. 2

Primary chemical metal plating:

Solution no. 1: 3 g of $CuSO_4 \cdot 5H_2O$, 3 g of $NiSO_4 \cdot 6H_2O$, 14 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 26 g of $NiSO_4 \cdot 6H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Electroplating: Copper plating bath Pragogal 2500, Pragochema a.s. Praha, Cu anode.

Characteristics: Specific surface resistance 0.4–0.6 Ω/square.

Fig. no. 2 shows an example of attenuation of electromagnetic radiation (axis Y in the range of 0 to 100 dB) with the above mentioned exemplary treated textile material depending on the radiation frequency (axis X in the range of 30 MHz to 1.5 GHz).

Example no. 3

Primary chemical metal plating:

Solution no. 1: 3 g of $CuSO_4 \cdot 5H_2O$, 3 g of $NiSO_4 \cdot 6H_2O$, 14 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 25 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Electroplating: Tin plating bath Pragogal 5500, Pragochema a.s. Praha, Sn anode.

Characteristics: Pure tin without a protective layer, specific surface resistance 0.9–1.3 Ω/square.

Example no. 4

Primary chemical metal plating:

Solution no. 1: 3 g of $CuSO_4 \cdot 5H_2O$, 3 g of $NiSO_4 \cdot 6H_2O$, 14 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 25 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Electroplating: Zinc plating bath Pragogal 3700, Pragochema a.s. Praha, Zn anode.

Characteristics: Pure zinc without a protective layer, specific surface resistance 1.0–1.3 Ω/square.

Example no. 5

Primary chemical metal plating:

Solution no. 1: 3 g of $CuSO_4 \cdot 5H_2O$, 3 g of $NiSO_4 \cdot 6H_2O$, 14 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 26 g of $NiSO_4 \cdot 6H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Electroplating: Nickel plating bath Pragogal 1051, Pragochema a.s. Praha, Ni anode.

Characteristics: Pure nickel without a protective layer, specific surface resistance 4.0–6.0 Ω/square.

Example no. 6

Primary chemical metal plating:

Solution no. 1: 3 g of $CuSO_4 \cdot 5H_2O$, 3 g of $NiSO_4 \cdot 6H_2O$, 14 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 0.5 g of $NiSO_4 \cdot 6H_2O$, 24.5 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Electroplating: no electroplating.

Characteristics: copper-nickel alloy (5.0% by weight of nickel), without a protective layer, surface resistance 5–7 Ω/square, 1.6 g of metal/m^2 of textile material, Cu precipitation 89.5%.

Example no. 7

Primary chemical metal plating:

Solution no. 1: 3 g of $CuSO_4 \cdot 5H_2O$, 3 g of $NiSO_4 \cdot 6H_2O$, 14 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 1.0 g of $NiSO_4 \cdot 6H_2O$, 24.0 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Electroplating: no electroplating.

Characteristics: copper-nickel alloy (6.7% by weight of nickel), without a protective layer, specific surface resistance 8–9 Ω/square, 1.6 g of metal/m^2 of textile material, Cu precipitation 90.1%.

Operating parameters of the continuous line according to the present invention used for Examples no. 8 to 9.

The input textile material is non-woven polyester textile with the width of 1.1 m and specific weight of 10 g/m^2. The unwinding and winding rate and travel speed of the textile material is 1 meter in a minute. The number of layers of the textile material to be metal plated is 3 layers. The chemical treatment is carried out in a bath with a composition of 100 g of NaOH and 15 ml of hydrogen peroxide (35%) per 1000 ml of demineralized water (DW) at the temperature of 60°C for 1 minute. The primary chemical metal plating proceeds in the range of 2 minutes (the length of the conveyor belt is 2 meters) in a protective atmosphere of nitrogen. The secondary chemical metal plating proceeds in the range of 5 minutes (the length of the conveyor belt is 5 meters). It is followed by overpressure dewatering and hot-air drying at 120°C for 2 minutes.

Example no. 8

Primary chemical metal plating:

Solution no. 1: 4 g of $CuSO_4 \cdot 5H_2O$, 2 g of $NiSO_4 \cdot 6H_2O$, 15 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 1.0 g of $NiSO_4 \cdot 6H_2O$, 24.0 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Characteristics: copper-nickel alloy (5.2% by weight of nickel), specific surface resistance 22.6–27.6 Ω/square, 0.57 g of metal/m^2 of textile material, Cu precipitation 93.8%.

Example no. 9

Primary chemical metal plating:

Solution no. 1: 2 g of $CuSO_4 \cdot 5H_2O$, 4 g of $NiSO_4 \cdot 6H_2O$, 10 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 6.5 g of $NiSO_4 \cdot 6H_2O$, 18.5 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Characteristics: copper-nickel alloy (19.2% by weight of nickel), specific surface resistance 34.4–36.3 Ω/square, 0.52 g of metal/m^2 of textile material, Cu precipitation 91.2%.

Operating parameters of the continuous line according to the present invention used for Example no. 10.

The input textile material is non-woven polyester textile with the width of 1.1 meters and specific weight of 10 g/m^2. Unwinding and winding rate and travel speed of the textile material 0.75 meters in a minute. The number of layers of the textile material to be metal plated is 3 layers. Chemical treatment in a bath with the composition of 100 g of NaOH and 15 ml of hydrogen peroxide (35%) per 1000 ml of demineralized water (DW) at the temperature of 60 °C for 1.3 minutes. Primary chemical metal plating in the range of 2.7 minutes (length of the conveyor belt 2 meters) in a protective atmosphere of nitrogen. Secondary chemical metal plating in the range of 6.6 minutes (length of the conveyor belt 5 meters). Overpressure dewatering and hot-air drying at 120 °C for 2.7 minutes.

Example no. 10

Primary chemical metal plating:

Solution no. 1: 6 g of $NiSO_4 \cdot 6H_2O$, 8 g of triethanolamine, 8 g of sodium hypophosphite per 1 liter of DW, pH 9.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 6.5 g of $NiSO_4 \cdot 6H_2O$, 18.5 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Characteristics: copper-nickel alloy (18.9% by weight of nickel), specific surface resistance 31.3–33.8 Ω/square, 0.54 g of metal/m^2 of textile material, Cu precipitation 92.4%.

Operating parameters of the continuous line according to the present invention used for Example no. 11.

The input textile material is non-woven viscose textile with the width of 1.1 m and specific weight of 45 g/m^2. Unwinding and winding rate and travel speed of the textile material 1.5 meters in a minute. The number of layers of the textile material to be metal plated is 1 layer. Primary chemical metal plating in the range of 1.3 minutes (length of the conveyor belt 2

meters) in a protective atmosphere of nitrogen. Secondary chemical metal plating in the range of 3.5 minutes (length of the conveyor belt 5 meters). Overpressure dewatering and hot-air drying at 180 °C for 2.2 minutes

Example no. 11

Primary chemical metal plating:

Solution no. 1: 5 g of $CuSO_4 \cdot 5H_2O$, 1 g of $AgNO_3$, 10 g triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 25 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Electroplating: Copper plating bath Pragogal 2500, Pragochema a.s. Praha, Cu anode.

Characteristics: Specific surface resistance 5.1–8.3 Ω/square, no electroplating 230.0–340.0 Ω/square.

Operating parameters of the continuous line according to the present invention used for Example no. 12.

The input textile material is viscose non-twisted endless fibers in the warp arrangement in the width of 1.1 meters. Unwinding and winding rate and travel speed of the textile material 1.0 meter in a minute. Primary chemical metal plating in the range of 2.0 minutes (length of the conveyor belt 2 m) in a protective atmosphere of nitrogen. Secondary chemical metal plating in the range of 5.0 minutes (length of the conveyor belt 5 meters). Overpressure dewatering and hot-air drying at 180 °C for 2.2 minutes

Example no. 12

Primary chemical metal plating:

Solution no. 1: 5 g of $CuSO_4 \cdot 5H_2O$, 1 g of $AgNO_3$, 10 g triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 25 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Characteristics: Specific resistance 1–3 kΩ/m.

Operating parameters of the continuous line according to the present invention used for Example no. 13.

The input textile material is non-woven polypropylene textile with the width of 1.1 meters and specific weight of 30 g/m^2. The unwinding and winding rate and travel speed of the textile material is 1 meter in a minute. The number of layers of the textile material to be metal plated is one layer. Plasma treatment with frequency corona under the conditions of 8 kHz, 20 kV and the power of 1 kW. Chemical treatment in a bath with the composition of 10 g of NaOH per 1000 ml of demineralized water (DW) for 1 minute. Primary chemical metal plating in the range of 2 minutes (length of the conveyor belt 2 meters) in a protective atmosphere of nitrogen. Secondary chemical metal plating in the range of 5 minutes (length of the conveyor belt 5 meters). Continuous electroplating in a constant current electroplating mode for 1 minute. Continuous wetting in the Pragokor Seal Cu protective varnish, overpressure dewatering and hot-air drying at 80 °C for 4 minutes.

Example no. 13

Primary chemical metal plating:

Solution no. 1: 3 g of $CuSO_4 \cdot 5H_2O$, 3 g of $NiSO_4 \cdot 6H_2O$, 14 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 25 g of $CuSO_4 \cdot 5H_2O$, 30 g of triethanolamine per 1 liter of DW, pH 9.5.

Solution no. 4: 2 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Electroplating: Copper plating bath Pragogal 2500, Pragochema a.s. Praha, Cu anode.

Characteristics: Specific surface resistance 0.4–0.6 Ω/square.

Operating parameters of the continuous line according to the present invention used for Example no. 14.

The input textile material is non-woven polyester textile with the width of 1.1 m and specific weight of 30 g/m^2. The unwinding and winding rate and travel speed of the textile material is 0.5 meter in a minute. The number of layers of the textile material to be metal plated is one layer. Plasma treatment with frequency corona under the conditions of 8 kHz, 13 kV and the power of 1 kW. The chemical treatment is carried out in a bath with the composition of 20 g of sodium hydroxide (NaOH) per 1000 ml of demineralized water (DW) for 1 minute. The

primary chemical metal plating proceeds in the range of 6 minutes in a protective barrier atmosphere against oxygen. The secondary chemical metal plating proceeds in the range of 4 minutes and electroplating realizes with the same time-out in an adjusted a constant current electroplating mode.

Example no. 14

Primary chemical metal plating:

Solution no. 1: 3 g of $CuSO_4 \cdot 5H_2O$, 3 g of $NiSO_4 \cdot 6H_2O$, 14 g of triethanolamine per 1 liter of DW, pH 8.5.

Solution no. 2: 0.5 g of $NaBH_4$, 1 g of NaOH per 1 liter of DW.

Secondary chemical metal plating:

Solution no. 3: 50 g of $CuSO_4 \cdot 5H_2O$, 70 g of triethanolamine per 1 liter of DW.

Solution no. 4: 4 g of $NaBH_4$, 4 g of NaOH per 1 liter of DW.

Electroplating: Copper plating bath Pragogal 2500, Pragochema a.s. Praha, Cu anode.

Characteristics: Based on conditions of constant current electroplating mode the electroplated textile is obtained with 9 to 11 g of metal/m^2 of textile material, a specific surface resistance 0.11 to 0.14 Ω/square. In the range of 55 MHz to 1.4 GHz attenuation of electromagnetic radiation exhibits values of 58 to 70 dB.

Although this invention has been described with reference to a certain particular embodiment, a number of other changes and modifications and further uses will be obvious to skilled persons. Therefore, the present invention is not restricted by the particular description by only by the appended patent claims.

LIST OF REFERENCE SYMBOLS

1 – unwinding and grouping device

2a – plasma device

2b – device for chemical cleaning or treatment

3 – unit for the primary chemical metal plating

4 – unit for the secondary chemical metal plating

5 – electroplating unit

6 – varnishing device

7 – ungrouping and winding device

8, 8′ – endless conveyor belts for the primary and secondary metal plating

9 – deactivation device of undesired metal plating

10, 10′ – application device

11, 11′ – belt device to eliminate the influence of atmospheric oxygen

12, 12′ – terminal device for cleaning of chemically metal plated textile material

References:

[1] Stremsdoerfer G. et al., Journal of Materials Science 38 (2003) 3285-3291

[2] Friedrich J., Winheim: Wiley-VCH 2012 xii, ISBN 978-3-527-31853-7

[3] Shishoo, R.: Boca Raton CRC Press, 2007, Woodhead Publishing in Textiles, ISBN 978-1-4200-4450-8

[4] Abouranayana H.M., Dowling D.P.: Surface Energy. InTech, 2015, ISBN 978-953-59-2216-6

[5] HANDBOOK of Electroplating Anodizing&Surface Finishing Technology (10th Edition 2015)

[6] HANDBOOK on Electroplating with Manufacture of Electrochemicals (2017)

[7] Pragochema a.s. Praha, corporate catalog

[8] Waterproof and Water Repellent Textiles and Clothing (1st Edition 2017)

CLAIMS

1. A method of continuous metal plating by unwinding and subsequent winding of metal plated textile material in full width, **characterized in that** it comprises the following steps:

under an inert gas atmosphere, or under a plastic foil barrier, textile material is subjected to the step of

primary chemical metal plating, which consists of:

- a reaction of the aqueous solution no. 1 of inorganic salts of metallic ions comprising, according to the periodic system of chemical elements, metals of group 11 (I. B group), groups 8, 9 and 10 (group VIII. B) – light platinum metals or the iron triad or their alloys or mixtures, containing an additive comprising primary, secondary and/or tertiary amines, in an aqueous alkaline medium, at a room temperature,
- with the aqueous solution no. 2 of a reductant comprising borohydrides of alkaline metals ($M^+BH_4^-$), hypophosphites of alkaline metals ($H_2PO_2^-$), derivatives of formaldehyde (HCHO), or hydrazine (N_2H_4) or their mixtures, in an aqueous alkaline medium,

to activate the surface of the textile material with adsorbed metal nanoparticles or their mixtures; and

subsequently, it is subjected to the step of

secondary chemical metal plating, which consists of:

- a reaction of the aqueous solution no. 3 of inorganic salts of metallic ions comprising, according to the periodic system of chemical elements, metals of group 11 (I. B group), or the iron triad or their alloys or mixtures, containing an additive comprising primary, secondary and/or tertiary amines in an aqueous alkaline medium ŧ,
- with the aqueous solution no. 4 of a reductant comprising borohydrides of alkaline metals ($M^+BH_4^-$), hypophosphites of alkaline metals ($H_2PO_2^-$), derivatives of

formaldehyde (HCHO), hydrazine (N_2H_4) or hydroxylamine (NH_2OH), their mixtures, in an aqueous alkaline medium,
to fill the 3D structure of the textile material with metals or their alloys.

2. The continuous metal plating method according to claim 1, **characterized in that** the continuous movement of textile material unwinding and winding proceeds at a synchronous rate of about 0.5 to 2 m/min in all the steps.

3. The continuous metal plating method according to claim 1 or 2, **characterized in that** the textile material is in the form of one integral layer or consisting of two to five material layers on each other, the sum of specific weight of individual layers being 100 g/m^2 at the most.

4. The continuous metal plating method according to one or more of claims 1 to 3, **characterized in that** the textile material comprises natural, synthetic or combined materials, fibrous woven, non-woven and knitted, flat textile materials and fibers of organic or inorganic origin or their mixture.

5. The continuous metal plating method according to claim 4, **characterized in that** the natural material is selected from the group comprising cotton, wool, silk, viscose, cellulose in general or their mixture.

6. The continuous metal plating method according to claim 4, **characterized in that** the synthetic textile material is selected from the group comprising polyester, polyethylene terephthalate, polybutylene terephthalate, polyamide, polyacrylate, polyurethane, polystyrene or glass or their mixture.

7. The continuous metal plating method according to claim 6, **characterized in that** the synthetic textile material is polyester composite non-woven textile.

8. The continuous metal plating method according to claim 4, **characterized in that** the synthetic textile material is selected from the group comprising polyethylene or polypropylene or their mixture.

9. The continuous metal plating method according to claim 4, **characterized in that** the combination of a natural and synthetic material is selected from the group comprising especially the combinations of cotton/polyester, wool/polyester, nylon/cotton or wool/polyamide.

10. The continuous metal plating method according to claim 1, **characterized in that** for the primary metal plating, the mutual molar ratio of the metal ion and amine of the aqueous solution no. 1 is in the range of 1:1 to 1:8, preferably 1:4 to 1:6.

11. The continuous metal plating method according to claim 1, **characterized in that** for the primary metal plating, the mutual volume ratio of the aqueous solution no. 1 to the aqueous solution no. 2 is 10:1 to 1:10, preferably 2:1 to 1:2 and most preferably 1:1.

12. The continuous metal plating method according to claim 1, **characterized in that** for the secondary metal plating, the mutual molar ratio of the metal ion and amine of the aqueous solution no. 3 is in the range of 1:1 to 1:4, preferably 1:2 to 1:3.

13. The continuous metal plating method according to claim 1, **characterized in that** for the secondary metal plating, the mutual volume ratio of the aqueous solution no. 3 to the aqueous solution no. 4 is 1:2 to 2:1.

14. The continuous metal plating method according to claim 1, **characterized in that** the metal ions of group 11 (I. B group) are ions of silver (Ag) or copper (Cu), the metal ions of groups 8, 9 and 10 (group VIII. B) are ions of palladium (Pd) and the metal ions of the iron triad are ions of nickel (Ni), cobalt (Co) or iron (Fe).

15. The continuous metal plating method according to claim 1, **characterized in that** the inorganic salts of the primary metal plating are selected from the group comprising sulfates, nitrates or perchlorates, preferably sulfates.

16. The continuous metal plating method according to claim 1, **characterized in that** the inorganic salts of the secondary metal plating are selected from the group comprising sulfates or hypophosphites.

17. The continuous metal plating method according to claim 1, **characterized in that** the additive for the primary as well as secondary metal plating is selected from ammonia (NH_3), ethanolamine ($NH_2C_2H_4OH$), diethanolamine ($(C_2H_4OH)_2NH$), triethanolamine ($(C_2H_4 OH)_3N$), propanolamine ($CH_3CH(OH)CH_2NH_2$), methylethanolamine ($CH_3NHC_2H_4OH$), dimethylethanolamine ($(CH_3)_2NC_2H_4OH$)), diethanolmethylamine ($CH_3 N(C_2H_4OH)_2$).

18. The continuous metal plating method according to one or more of claims 1 to 17, **characterized in that** the step of primary and secondary metal plating is followed by the step of cleaning by suction of residues of the metal plating solutions with the subsequent step of rinsing of the textile material with demineralized/deionized water and suction of any excess of this water.

19. The continuous metal plating method according to one or more of claims 1 to 18, **characterized in that** the step of primary metal plating is preceded by the step of chemical treatment of the textile material with 1 to 20% by weight solution of an alkaline metal hydroxide in demineralized/deionized water at a temperature of 55–85 °C.

20. The continuous metal plating method according to claim 19, **characterized in that** the alkaline metal hydroxide further comprises peroxides or peroxo-salts of inorganic acids and/or hydrogen peroxide.

21. The continuous metal plating method according to claims 1 and 8, **characterized in that** before the step of chemical treatment of the textile material, the material is subject to the step of physical treatment with a plasma discharge.

22. The continuous metal plating method according to claim 21, **characterized in that** the plasma discharge consists of a high-frequency discharge between two electrodes separated by at least one dielectric with inserted voltage of up to 80 kV and frequency of up to 20 kHz, at a power of 400 to 2000 W and is applied under atmospheric conditions.

23. The continuous metal plating method according to one or more of claims 1 to 22, **characterized in that** the textile material is subjected to electroplating in an electroplating bath with replenishment of the anode metal and a cathode, which is the textile material to be chemically metal plated.

24. The continuous metal plating method according to claim 23, **characterized in that** the anode metal is selected from the group comprising gold (Au), silver (Ag), nickel (Ni), cobalt (Co), copper (Cu), tin (Sn), zinc (Zn), indium (In), bismuth (Bi) and chromium (Cr) or their alloys, the electroplating bath consisting especially of aqueous solutions of chlorides or sulfates of the said metals.

25. The continuous metal plating method according to one or more of claims 1 to 24, **characterized in that** the metal plated material is fitted, on at least a part of its surface, with protective varnish or glazing by immersion, under continuous movement of this metal plated material, in a bath with water-dilutable dispersion and emulsion varnish based on highly hydrophobic fluorocarbon polymers of type C8 or C6, or lubricants based on sodium alkyl thiolates, or formulated with the presence of nanoparticles, with a subsequent step of treatment on rollers, then subjected to the step of vacuum suction of excessive varnish of lubricant with the final step or final hot-air drying at a temperature of about 80 to 200_°C for 2–15 minutes.

26. The continuous metal plating method according to claim 25, **characterized in that** the viscosity and concentration of the varnish or lubricant is selected in such a way to reduce air permeability of the finished metal plated textile material as compared to unvarnished material by 10% at the most.

27. Device for execution of the method according to one or more claims 1 to 26, **characterized in that** it comprises the following units arranged consecutively in a continuous line:

a) an unwinding and grouping device (1) of textile material, which is followed by
b) a device (2a) for physical treatment of textile material with plasma wherein after this device,
c) a device (2b) for chemical treatment of the said material is arranged, and after it

d) a unit (3) for the primary chemical treatment of textile material, together with cleaning of the metal plating belt, is arranged, which is followed by

e) a unit (4) for the secondary chemical treatment of textile material, together with cleaning of the metal plating belt, and subsequently

f) an electroplating unit (5) of textile material is arranged, which is followed by

g) a unit (6) of varnishing the metal plated textile material, which is finally followed by

h) an ungrouping and winding device (7) of the metal plated textile material.

28. The device according to claim 27, characterized in that it further comprises a device for central mixing of the reaction solutions 1, 2, 3 and 4 with an adjacent application device (10, 10′) for static or dynamic application of these reaction solutions by injection, spreading or with a slot die onto the moving textile material.

29. The device according to claim 27 or 28, **characterized in that** the design of the unit (3) and unit (4) is based on a pair of endless conveyor belts (8, 8′), which are transversally and horizontally horizontal, and in the form of a belt device (11, 11′) to eliminate the influence of atmospheric oxygen, which is transversally and longitudinally horizontal, situated vertically above each other in such a way that the textile material and reaction solutions 1, 2, 3 and 4 are tightly compressed between the conveyor belts (8, 8′) and the belt devices (11 a 11′), the movement of which is synchronized.

30. The device according to claim 29, **characterized in that** at the outer sides of the endless conveyor belts (8, 8′) and the belt devices (11, 11′), deactivation devices (9) are attached to continuously remove undesired metal plating of the conveyor belts (8, 8′) and the belt devices (11, 11′), comprising a solution of nitric acid, and for their subsequent final cleaning, terminal devices (12, 12′) with demineralized/deionized water.

31. Metal plated textile material, **characterized in that** the specific contents of metals achieve 0.52 g of metal/m^2 to 11 g of metal/m^2 of the textile material and the specific surface resistance is 0.1 to 40 Ω/square.

32. Use of the metal plated textile material according to claim 31 to enhance the absorption and reflectivity of electromagnetic radiation, electrical and thermal conductivity, and antibacterial and antifungal characteristics.

FIG. 1

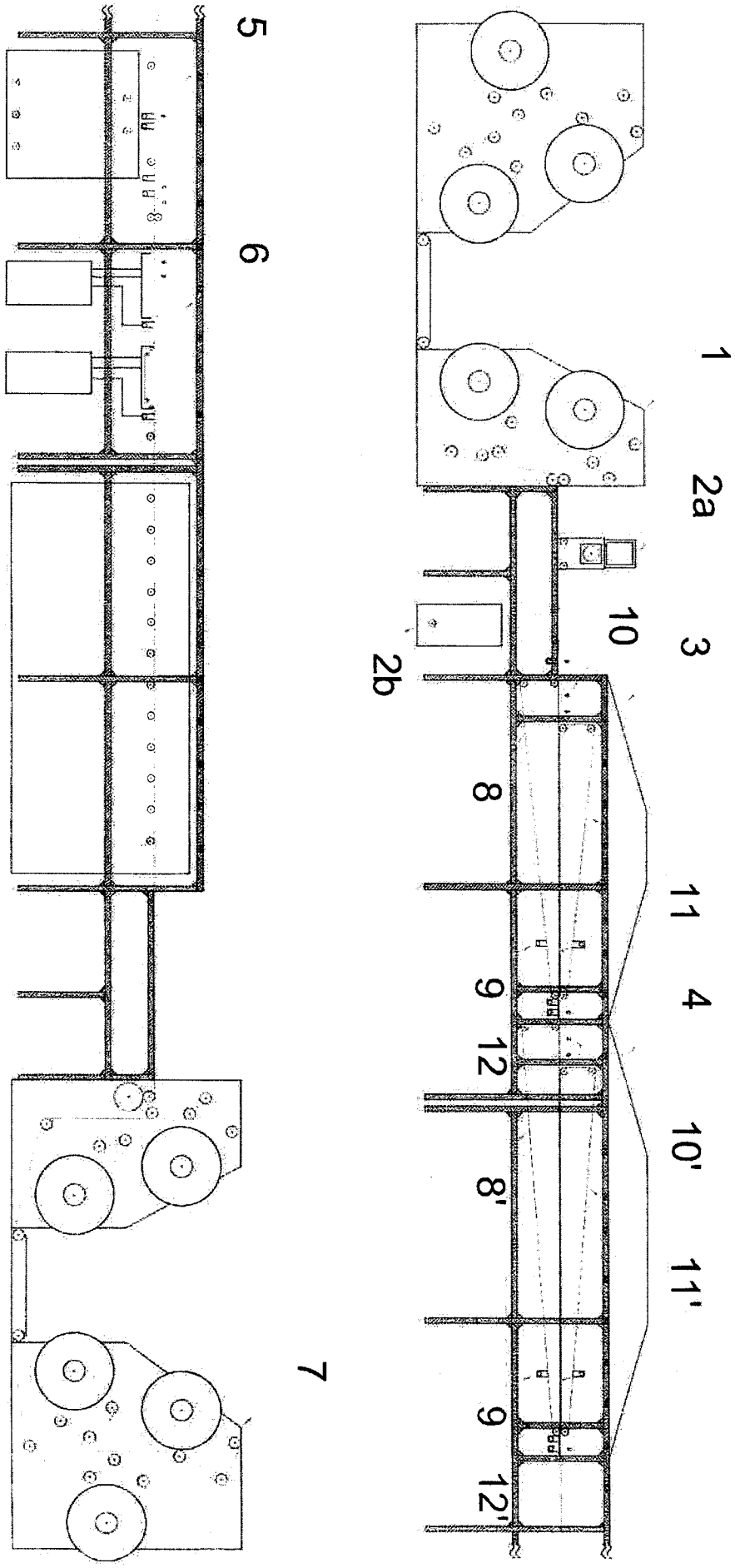
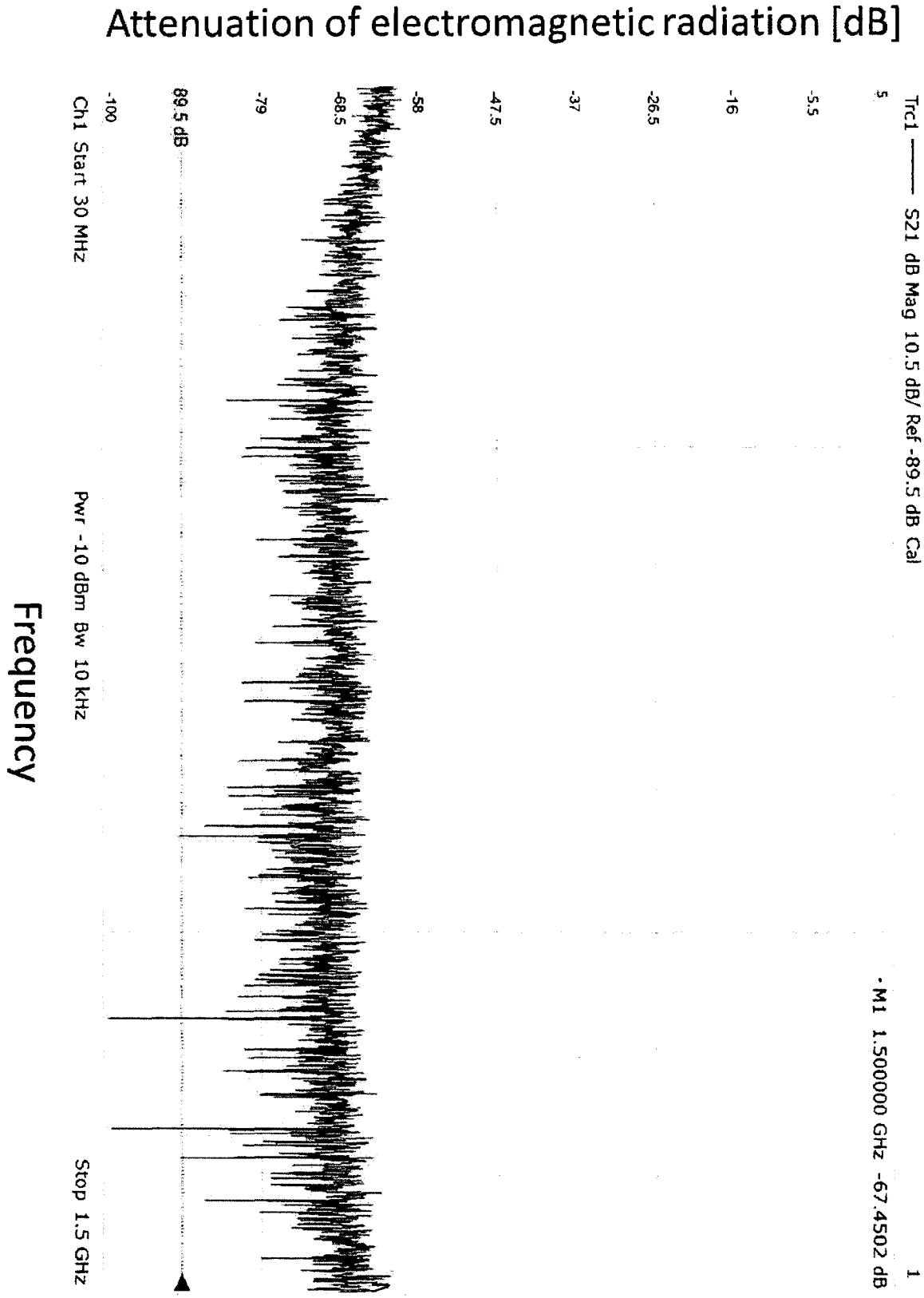


FIG. 2


Attenuation of electromagnetic radiation [dB]
Trc1 S21 dB Mag 10.5 dB/ Ref -89.5 dB Cal
5
-5.5
-16
-26.5
-37
-47.5
-58
-68.5
-79
-89.5 dB
-100
Ch1 Start 30 MHz
Pwr -10 dBm Bw 10 kHz
Stop 1.5 GHz
M1 1.500000 GHz -67.4502 dB
1
Frequency

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2019/000053

A. CLASSIFICATION OF SUBJECT MATTER
INV. D06M11/83 C23C18/16 C23C18/18 C23C18/20 C25D7/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D06M D06Q

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 9 284 645 B2 (STREMSDOERFER SAMUEL [FR]; JET METAL TECHNOLOGIES [FR]) 15 March 2016 (2016-03-15) cited in the application claims 1-8 column 4, lines 50-57 column 6, lines 19-46 column 7, lines 27-49 figure 2 column 4, lines 11-15 ----- -/--	1-32

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 February 2020	25/03/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Barathe, Rainier

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2019/000053

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/128505 A1 (SEC DEP FOR BUSINESS INNOVATION & SKILLS [GB]) 28 August 2014 (2014-08-28)	1-32
Y	page 7, paragraph 5 page 8 last but one paragraph figure 4 page 11, paragraph 3-4 examples 1-4 page 13 last paragraph claims	1-32

X	WO 02/02861 A1 (EXPAN ELEC CO LTD [KR]; CHOI CHUL SOO [KR]; KIM SUN KI [KR]) 10 January 2002 (2002-01-10) figure 5 page 7, lines 2-14	31,32

X	CZ 31 290 U1 (TECHNICKÁ UNIVERZITA V LIBERCI [CZ]; VECERNÍK S R O [CZ]) 20 December 2017 (2017-12-20) claim 5	31,32

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/CZ2019/000053

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 9284645 B2	15-03-2016	AU 2009275851 A1	04-02-2010
		BR PI0916730 A2	10-11-2015
		CA 2731407 A1	04-02-2010
		CN 102144045 A	03-08-2011
		EG 27060 A	05-05-2015
		EP 2326747 A2	01-06-2011
		ES 2538791 T3	24-06-2015
		FR 2934609 A1	05-02-2010
		JP 5703214 B2	15-04-2015
		JP 2011529528 A	08-12-2011
		KR 20110044885 A	02-05-2011
		MA 32549 B1	01-08-2011
		MY 158289 A	30-09-2016
		PL 2326747 T3	31-08-2015
		PT 2326747 E	16-07-2015
		RU 2011107716 A	10-09-2012
		SI 2326747 T1	30-10-2015
		US 2011155444 A1	30-06-2011
		WO 2010012810 A2	04-02-2010
WO 2014128505 A1	28-08-2014	AU 2014220444 A1	10-09-2015
		CA 2902278 A1	28-08-2014
		CN 105189851 A	23-12-2015
		EP 2959053 A1	30-12-2015
		ES 2688053 T3	30-10-2018
		JP 6348518 B2	27-06-2018
		JP 2016513182 A	12-05-2016
		KR 20160008501 A	22-01-2016
		PL 2959053 T3	31-12-2018
		RU 2015138489 A	30-03-2017
		US 2016010273 A1	14-01-2016
		WO 2014128505 A1	28-08-2014
WO 0202861 A1	10-01-2002	AU 4121801 A	14-01-2002
		CN 1446280 A	01-10-2003
		DE 10196402 T1	05-06-2003
		JP 2004502055 A	22-01-2004
		US 2003102225 A1	05-06-2003
		WO 0202861 A1	10-01-2002
CZ 31290 U1	20-12-2017	CZ 31290 U1	20-12-2017
		WO 2019072322 A1	18-04-2019