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(54) METHOD FOR APPLYING A LINING FOR FERROUS AND NON-FERROUS METAL WIRES AND CABLES AND THEIR ALLOYS

(57) Disclosed herein is a method using ultraviolet radiation to form a solid polymeric coating on a surface of wires of ferrous and non-ferrous metal and their alloys with homogeneous section of any shape and size and cables formed by stranded wires, characterised in that it comprises the steps of:

- application: coating the surface of wires and cables with a compound in liquid state or in the form of powders and solid particles of various size and shape, which is constituted by monomers and/or oligomers and/or polymers, as well as additives and photoinitiators;
- curing: exposing the previously applied compound to an amount of ultraviolet radiation, with one or more wavelengths, sufficient to react the photoinitiators and to trigger the cross-linking polymerisation which causes the curing of the compound and therefore forms the polymeric coating and having flexibility, elongation, curing and adherence features such as to ensure high protective capacities.

The method applies to protective, decorative or lubricating coatings.

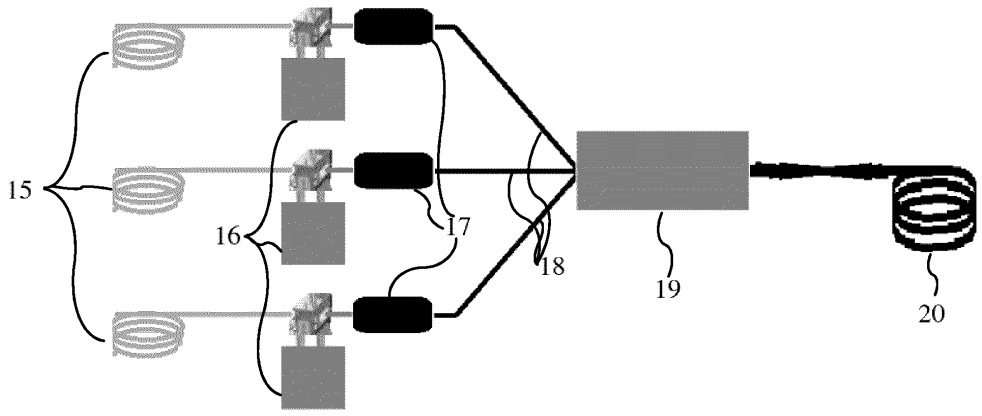

FIG. 4

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Description

Field of the Invention

[0001] The present invention relates to a method for forming a solid polymeric coating on the surface of metal wires with a section of any shape and size and cables formed by stranded wires. Said method includes a first step of application of the liquid or solid state compound and a second step of curing such compound through the application of an amount of ultraviolet radiation, sufficient to trigger the cross-linking polymerisation which causes the solidification of the compound and the consequent formation of a coating with features of flexibility, elongation, hardness and adhesion, such as to ensure high protective capacity and/or with lubricant features.

Previously used techniques

[0002] Coatings are used to decorate wires and cables and to protect them from deterioration factors, deriving from oxidation, from chemical and environmental agents, such as corrosion in marine environments, as well as by other aging factors, prolonging the useful life of the wires and cables themselves.

[0003] Wires and cables coatings may also have other purposes. An example is that of the drawing and/or rolling of metal (ferrous or non-ferrous) and their alloys wire rod and/or wire, having sections of any shape or size. This process, known since a long time, consists in reducing the section of the wire rod and/or wire by deformation, without removing any material.

[0004] According to a first method, the rod and/or the wire is passed inside of arrays of material of appropriate hardness, commonly called dies, the section of which negatively reproduces the shape and the size of the cross section of the wire rod and/or wire to be obtained. One or more steps can be provided through the dies and through one or more machines. These steps create friction on the wire rod or on the wire, with consequent heating of these and with possible consequent breakages. For this reason, the surface of the wire rod and/or the wire must be lubricated, so as to reduce the friction and therefore the heating and the breakage. For this purpose, lubricants are generally used, such as stearates, which are solid at room temperature (dry lubrication), or oils that are liquids (bath lubrication). The dry lubricant is applied on the wire rod and/or on the wire, while bath lubrication involves dipping the die into the lubricant.

[0005] According to a second method, called rolling, the wire rod and/or the wire are deformed by rollers which exert a mechanical pressure on the wire rod and/or wire. In this case, only dry lubrication occurs, similarly to what has already been seen for the first method.

[0006] These techniques involve significant harmful emissions, especially of dust, in the environment, with risks for the safety and health of the operators.

[0007] Another purpose is to limit corrosion and deterioration of the wire rod and/or wire, protecting them from air and moisture with a barrier effect.

[0008] The polymeric compounds used nowadays for these purposes are self-supporting plastic coatings, made by applying to the surface powders and/or polymerising materials, which are subsequently solidified by means of a thermal process. The execution of this thermal curing process requires the use of bulky and expensive systems.

[0009] Other coatings for wires and cables used nowadays, other than polymeric ones, use solvent-based protective paintings, also cured and transformed into a solid coating by means of a thermal process. The execution of this thermal curing process also requires the use of bulky and expensive plants and is related to significant atmospheric emissions of volatile organic compounds (VOCs) originating environmental impacts and significant risks for the health of the workers, associated to inhalation of these vapours.

[0010] Other coatings for wires and cables used nowadays, different than polymeric ones, use metals, such as zinc, nickel, copper, aluminium and their alloys, transformed into coatings through processes of dipping in fused baths or fluidised beds, or by electrochemical action. The execution of these processes requires the use of bulky and expensive systems and the industrial processes implemented in these systems generate significant environmental problems, linked to the use of heavy metals and their transformation into processing residues (acids, sludges, other special residues), hazardous to health and of problematic disposal.

[0011] The object of the present invention is to provide a coating of metal wires, cables or wire rods, both for decorative purposes and for protective purposes, as well as lubricant for drawing, rolling or similar processes and, at the same time, clearing the VOC emission, whilst also avoiding the formation of industrial waste, to be achieved with less bulky equipment and systems, characterised by a low initial economical investment and low costs in terms of energy resources.

[0012] In addition, the times of application and solidification of the compound must be strictly limited and allow a production speed higher than that of the described systems. This can be achieved with a method for the formation of a solid polymeric coating on a surface of wires of ferrous and non-ferrous metal and of their alloys with homogeneous section of any shape and size and cables formed by stranded wires, characterised in that it includes the steps of:

- application: coating the surface of wires and cables with a compound in liquid state or in the form of powders and solid particles of various size and shape, constituted by monomers and/or oligomers and/or polymers, as well as additives and photoinitiators;
- curing: exposing the previously applied compound to an amount of ultraviolet radiation, with one or more wavelengths, which is sufficient to react the photoin-

itiators and to trigger the cross-linking polymerisation which causes the curing of the compound and therefore forms the polymeric coating. According to a first aspect, said coating is a layer of decoration and/or protection, while, according to a second aspect, said coating is a lubricant for drawing or rolling.

Description of the Drawings

[0013] Further features of the method of the invention claimed are apparent from the following description, which contains the references to some preferred industrial embodiments thereof, given by way of example and explained by referring to the drawings contained in the attached document, without having the purpose of limiting in any way the scope of protection of the present invention. As already specified above, other embodiments can be realised with modifications of detail, within the spirit and scope of the claims.

[0014] In particular, the wires and cables are presented in the form of a coil, both inbound and outbound from the process: not excluding different possibilities, such as the application of the coating on the wires and cables of rectilinear shape.

[0015] In addition, the operating units are presented graphically in a separated manner. It is reiterated that the method of which the invention is claimed is realised through an industrial process in two sequential steps, by passing the wire or cable inside of two or more serial operating units, one or more for each step, or within one or more operating units within each of which the two steps are carried out in sequence. This graphical representation therefore has the only purpose to represent the process in a simple way, to help understanding the description.

Figure 1: cross-linking polymerisation of a wire coating in line with the drawing operation.

Figure 2: cross-linking polymerisation of a wire coating not in line with the drawing operation.

Figure 3: cross-linking polymerisation of a wire coating not in line with the drawing operation with application of the coating in the vertical direction.

Figure 4: cross-linking polymerisation of a coating of a wire or of a cable in line and upstream of mechanical forming process of the cable.

Figure 5: cross-linking polymerisation of a coating of a cable in line and downstream of the mechanical forming process of the cable.

Figure 6: cross-linking polymerisation of a coating of a cable not in line with the mechanical forming process.

Figure 7: cross-linking polymerisation of a coating in vertical direction, not in line with the mechanical forming process.

Figure 8: represents the polymerisation on a wire rod or on a wire of a single layer lubricating coating in line, on a machine for drawing and/or rolling.

Figure 9: represents the polymerisation on a wire rod or wire in line on a machine for drawing and/or rolling of a multiple coating.

Figure 10: represents the polymerisation of a lubricating coating in vertical.

Figure 11: represents the polymerisation of a lubricating coating in horizontal.

Detailed Description

[0016] The method for which the invention is claimed is achieved through an innovative industrial process, which has never been applied to metal wires or cables, nor to wire rods.

[0017] The industrial applications of the invention relate to the coating of wires and cables used in multiple fields of industrial production, in order both to ensure high standards of protection of the wires and cables from deterioration factors, such as oxidation and the corrosive action of chemical and environmental agents, and to obtain decorating colouring of the surface, and to superficially apply a lubricant for the subsequent processing (extrusion, rolling, etc.).

[0018] The process comprises two sequential operational steps, passing the wire or cable inside two or more serial operating units, one or more for each step, or within one or more operating units, within each of which the two steps are carried out in sequence.

[0019] The first step consists in the physical application of a compound on the outer surface. This application is obtained by passing the wire or the cable in the operating units where the operation took place in a manner known per se. Preferably, the wire or cable runs inside of machines and production lines, adapted to perform the two steps, without the constraints of direction, if not those determined by the layout of the machines and of the production lines themselves.

[0020] The compound is formed from monomers and/or oligomers and/or polymers and/or other additives and photoinitiators, it is present in liquid or solid form (powders and solid particles of various size and shape) and is applied to the wire or to the cable with different techniques, known per se.

[0021] As the compound to be applied in the first step, one or more may preferably be chosen among (the compounds in brackets are just some examples of compounds belonging to the general categories): oligomers (acrylated urethanes, acrylated polyesters, aliphatic and aromatic epoxy acrylates, unsaturated polyesters, amino functionalised acrylated oligomers, silicone acrylates) monomers (low molecular weight acrylates, vinyl ethers, vinyl esters, propenyl esters, acrylic acid, vinyl phosphonates, vinyl sulfonic acid, fumaric acid, itaconic acid, thiols), photoinitiators, synergists (amines, boranes, thiols, silanes), organic and inorganic pigments, fillers and additives (silica nanoparticles, alumina, sucrose benzoate, boron nitride, polyolefin waxes, metal soaps, zinc stearate, aluminium stearate, polytetrafluoroethylene, graph-

ite, borax pentahydrate, molybdenum, calcium stearate, sodium stearate), antioxidants and stabilisers. All these compounds have a high capacity of polymerisation and cross-linking when irradiated with light of appropriate wavelengths and, under such conditions, do not release volatile substances harmful to health and to the environment. In addition, polymers that are obtained have a high capacity of corrosion protection and lubrication.

[0022] If the compound is present in the liquid state, it is applied by directly contacting the wire or cable with the compound in the liquid state and calibrated through one or more dies, to obtain a uniform thickness on the surface using the following industrial technologies: passage through one or more dies, vacuum applicators, spray systems, mats, roller applicators, pressure dies, all easily available, having a reasonable encumbrance and often already present at the company premises.

[0023] If the compound is in the solid state, it is applied by directly contacting the wire or cable with the compound in the solid state in the form of powders and solid particles of various shapes and sizes and calibrated through one or more dies, to obtain a uniform thickness on the surface using industrial technologies known such as, but not limited to: passage through one or more dies, application of electrostatic charge to the wire or cable, passage through one or more pressure dies, fluidised beds, all easily available, having a reasonable encumbrance and often already present in the company.

[0024] The second step consists in the cross-linking polymerisation of the compound applied with the previously disclosed modes. The cross-linking polymerisation transforms the compound applied in a solid polymer, the composition of which allows to ensure high standards of protection of the wires and cables from deterioration factors derived from oxidation, from chemical and environmental factors, for example corrosion in marine environments, as well as from other aging factors, thereby extending their useful life. Different compounds are applied for specific protection requirements. Alternatively, such polymers can have high lubricating capacity, allowing the coated material to undergo the main machining operations without overheating or breakages.

[0025] This coating is transparent or coloured. The decorative aspect results from the possibility to use the compounds of various colours.

[0026] The cross-linking polymerisation is obtained by irradiating the wire or the cable or the wire rod, coated during the first step, with ultraviolet radiation generated by one or more radiating elements, possibly with the aid of reflectors that allow to optimise the irradiation and that use industrial technologies, such as arc technology, microwave technology, LED technologies. Preferably, said ultraviolet light has a wavelength ranging between 150 and 400 nm, most preferably between 250 and 400 nm. Within these ranges, the polymerisation is very fast.

[0027] The cross-linking polymerisation can be facilitated by limiting the presence of oxygen through the use of inert gases in the environment where the radiation takes place and the consequent cross-linking polymerisation reaction, since oxygen is an inhibitor of such a reaction.

[0028] Ultraviolet radiation, even within the ranges previously defined, can have different wavelengths even within a single cross-linking polymerisation process. This is linked to the type of photoinitiators chosen and ultimately to the features to be obtained for the coating.

[0029] In a preferred embodiment, the process of application and curing of the compound for forming the coating occurs in an environment where inert gases are present in high percentage, so as to obtain optimum results.

[0030] In a preferred embodiment, the metal wire or cable enters a tunnel, wherein the ultraviolet radiation irradiate the compound surface by 360°. In a very short time (from 0.1s to 10s) the components of the polymer compound react with the free radicals from the photoinitiators, triggering the cross-linking polymerisation.

[0031] Examining the drawings in detail, it is noted that in fig. 1, which is a schematic view of a preferable embodiment, relating to the application of the coating on a metal wire immediately downstream of the drawing process, the uncoated wire or wire rod (1) in form of a coil passes through any type and kind of drawing machine (2), is drawn (3), is passed inside the operating unit where the compound (4) is applied and immediately enters the operating unit where the cross-linking polymerisation induced by ultraviolet radiation (5) occurs, then the coated wire is rewound into coils (6), according to a known mechanical process.

[0032] Regarding fig. 2, it is a schematic view of a preferred embodiment, regarding the application of a coating on a metal wire in the form of coil wire, already previously drawn. The coil of uncoated metal wire (7) is passed inside the operating unit where the compound (8) is applied and immediately enters the operating unit where the cross-linking polymerisation induced by ultraviolet radiation (9) occurs, then the coated wire is rewound in coils (10), according to a known mechanical process.

[0033] Fig. 3 is a schematic view of a preferred embodiment, regarding the application of a coating on a metal wire in the form of wire coils, already previously drawn. The coil of uncoated wire (11) is passed in vertical direction inside the operating unit where the compound (12) is applied and immediately enters the operating unit where the cross-linking polymerisation induced by ultraviolet radiation (13) occurs, then the coated wire is rewound in coils (14), according to a known mechanical process.

[0034] Turning now to fig. 4, it is a schematic view of a preferable embodiment, concerning the application of the coating on a wire or a cable, wherein the wire or cable in the form of coil (15) is made to pass inside the operating unit where the compound (16) is applied and immediately enters the operating unit where the cross-linking polymerisation, induced by ultraviolet radiation (17), occurs. Then the coated wires or cables (18) undergo the process

of final mechanical forming cable (19) which is rewound in coils (20), according to a mechanical process known.

[0035] In turn, fig. 5 is a schematic view of a preferable embodiment, relating to the application of the coating downstream of the wire forming process, wherein a wire in form of a coil (21) is mechanically formed (22) and is passed inside the operating unit where the compound (23) is applied and immediately enters the operating unit where the cross-linking polymerisation induced by ultraviolet radiation (24) occurs, then the coated wire is rewound into coils (25) according to a known mechanical process.

[0036] Fig. 6 is a schematic view of a preferred embodiment, regarding the application of the coating on a metal cable in coil. The coil of uncoated metal cable (26) is passed inside the operating unit where the compound (27) is applied and immediately enters the operating unit where the cross-linking polymerisation induced by ultraviolet radiation (28) occurs, then the coated cable is rewound in coils (29) according to a known mechanical process.

[0037] In fig. 7, there is a schematic view of a preferred embodiment, regarding the application of a coating on a metal cable in the form of coil. The coil of uncoated metal cable (30) is passed in vertical direction inside the operating unit where the compound (31) is applied and immediately enters the operating unit where the cross-linking polymerisation induced by ultraviolet radiation (32) occurs, then the coated cable is rewound in coils (33), according to a known mechanical process.

[0038] In fig. 8 a schematic view of a preferred embodiment is seen, relating to the application of a lubricating coating. The application of the layer of lubricant occurs immediately upstream of the process of drawing and/or rolling, by passing the wire 1 in the operating unit where the coating 2 is applied. Immediately thereafter, it enters the operating unit 5, where a source of UV starts the cross-linking polymerisation. The wire 1 then passes through a die 4 and is drawn or rolled (5). The wire is then wound in coils (6) . In practice, the industrial process of application and curing of the compound to form the coating is performed in line with the process of drawing of the wire. However, it is also possible to operate in such a way that the industrial process of application and curing of the compound for forming the coating is not performed in line with the drawing process of the wire.

[0039] In fig. 9 it can be seen that, for each die upstream of which it is decided to apply the lubricating coating, the wire rod or wire 7 is passed through the unit 8 where the coating is applied and then, immediately afterwards, into the unit 9, where a source of UV starts the cross-linking polymerisation. The wire 7 then passes through an extruder 10, exits in 34 to form the coils 35. In practice, the industrial process of application and curing of the compound is performed several times, in order to achieve a coating formed by multiple overlapped layers.

[0040] In fig. 10, the uncoated wire rod and/or wire 11 is passed in a vertical direction inside the unit 12 where the lubricating coating is applied and then enters the operating unit 13, where a UV source activates the polymerisation, then the wire is wrapped in coils 14 and is thus stored.

[0041] The drawing and/or rolling can be carried out in a second moment, picking up the wire rod and/or the wire from a warehouse 36 and proceeding, in the unit 37, to the drawing and/or rolling. The wire is then wound in coils 38.

[0042] Finally, in fig. 11, the wire rod and/or wire 39 is made to pass in a vertical direction, inside a production unit 40, where the lubricating coating is applied. Subsequently, it enters the operating unit 41, where cross-linking polymerisation occurs, induced by UV rays, then the wire is wound in coils 42 and stored.

[0043] The drawing and/or rolling can be performed at a later time, by taking wire rod and/or wire from the warehouse 43, proceeding to drawing or rolling at 44 and winding the wire in coils at 45.

[0044] It can be expected that the industrial process of application and curing of the compound to form the coating is applied to a cable formed by a bundle of cables.

[0045] Finally, the process of application and curing of the compound to form the coating may also be applied to wires and cables, already previously coated.

Claims

1. Method for the formation of a solid polymeric coating on a surface of wires of ferrous and non-ferrous metal and of their alloys with homogeneous section of any shape and size and cables formed by stranded wires, **characterised in that** it comprises the steps of:

   - application: coating the surface of wires and cables with a compound in liquid state or in the form of powders and solid particles of various size and shape, constituted by monomers and/or oligomers and/or polymers, as well as additives and photoinitiators;
   - curing: exposing the previously applied compound to an amount of ultraviolet radiation, with one or more wavelengths, sufficient to react the photoinitiators and to trigger the cross-linking polymerisation which causes the curing of the compound and therefore forms the polymeric coating.

2. Method according to claim 1, **characterised in that** the wire and cable run inside of machines and production lines, adapted to carry out the two steps, without the constraints of direction except those determined by the layout of the machines and production lines themselves.

3. Method according to claims 1 or 2, **characterised in that** the industrial process of application and cur-

ing of the compound is performed several times, in order to achieve a coating formed by multiple overlapped layers.

4. Method according to any one of claims 1 to 3, **characterised in that** the step of application is carried out by directly contacting the wire or cable with the compound in liquid state and calibrated to obtain a uniform thickness on the surface using the following industrial technologies: passage through one or more dies, vacuum applicators, spray systems, mats, roller applicators or pressure dies.

5. Method according to any one of claims 1 to 3, **characterised in that** the step of application is carried out by directly contacting the wire and cable with the compound in solid state in the form of powders and solid particles of various shapes and sizes and calibrated to obtain a uniform thickness on the surface using industrial technologies such as: passage through one or more dies, application of electrostatic charge to the wire and cable, fluidised beds.

6. Method according to any one of the preceding claims, **characterised in that**, as a compound to be applied in the first step, it can be preferably choosen among one or more of: oligomers (acrylated urethanes, acrylated polyesters, aliphatic and aromatic epoxy acrylates, unsaturated polyesters, amino functionalised acrylated oligomers, silicone acrylates) monomers (low molecular weight acrylates, vinyl ethers, vinyl esters, propenyl esters, acrylic and methacrylic acid, vinyl phosphonates, vinyl sulfonic acid, fumaric acid, itaconic acid, thiols), photoinitiators, synergists (amines, boranes, thiols, silanes), organic and inorganic pigments, fillers and additives (silica nanoparticles, alumina, sucrose benzoate, boron nitride, polyolefin waxes, metal soaps, zinc stearate, aluminium stearate, polytetrafluoroethylene, graphite, borax pentahydrate, molybdenum, calcium stearate, sodium stearate), antioxidants and stabilisers.

7. Method according to any one of the preceding claims, **characterised in that** the step of curing the compound is carried out through ultraviolet radiations, generated by one or more irradiators that use industrial technologies, such as: arc technology, microwave technology, LED technology.

8. Method according to any one of the preceding claims, **characterised in that** the industrial process of application and curing of the compound to form the coating is performed in line with the process of drawing of the wire.

9. Method according to any one of claims 1 to 7, **characterised in that** the industrial process of application and curing of the compound to form the coating is not performed in line with the drawing process of the wire.

10. Method according to any one of the preceding claims, **characterised in that** the industrial process of application and curing of the compound to form the coating is applied to a cable formed by a bundle of cables.

11. Method according to any one of the preceding claims, **characterised in that** the process of application and curing of the compound to form the coating is applied to wires and cables, already previously coated.

12. Method according to any one of the preceding claims, **characterised in that** the process of application and curing of the compound to form the coating takes place in an environment where inert gases are present in high percentage.

13. Method according to any one of the preceding claims, **characterised in that** said coating is a decoration and/or protection layer.

14. Method according to any one of claims 1 to 12, **characterised in that** said coating is a lubricant for drawing or rolling.

15. Method as in any one of the preceding claims, **characterised in that** said ultraviolet light has a wavelength ranging between 150 and 400 nm, most preferably between 250 and 400 nm.

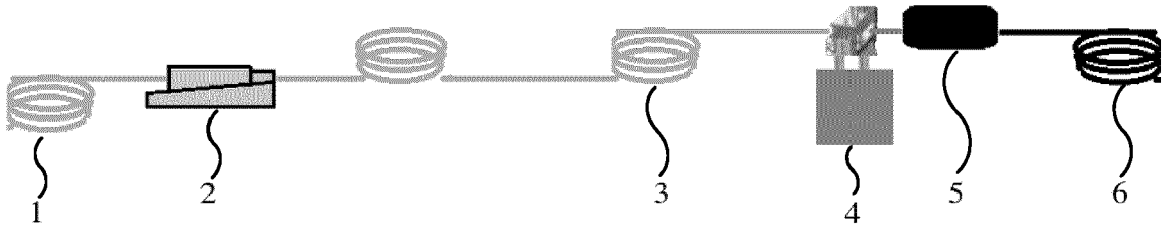

FIG. 1

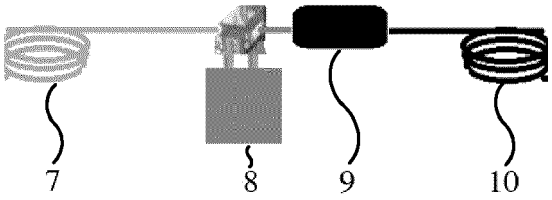

FIG. 2

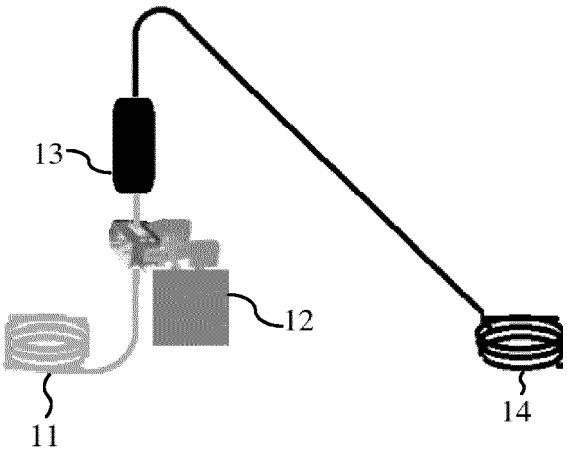

FIG. 3

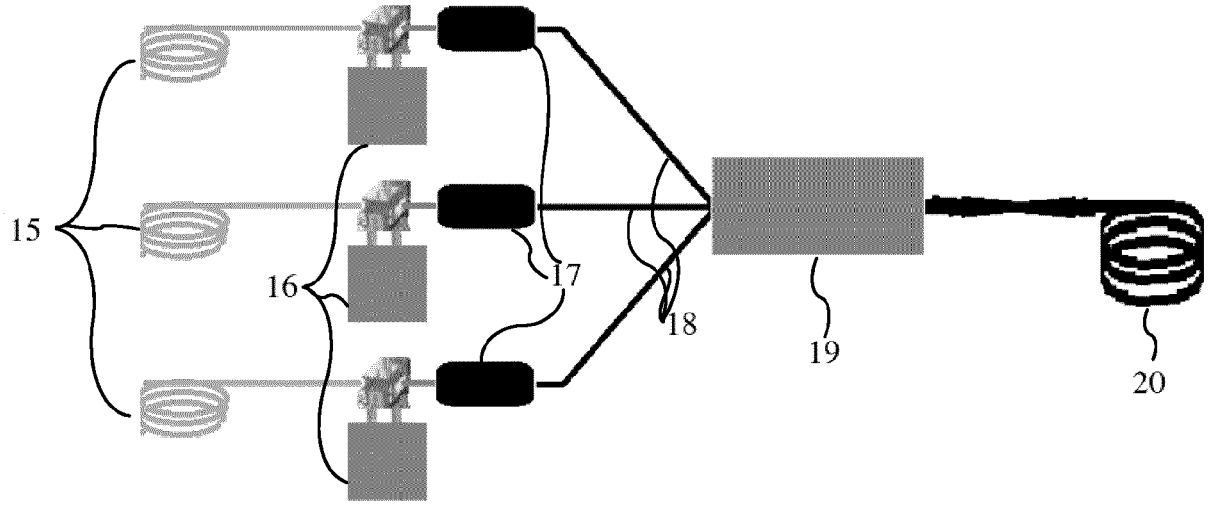

FIG. 4

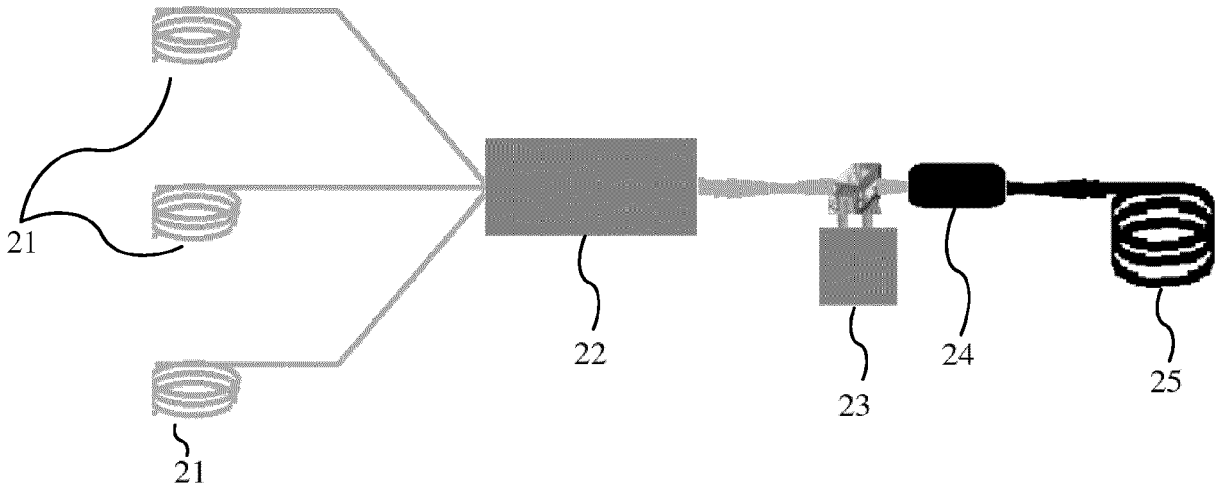

FIG. 5

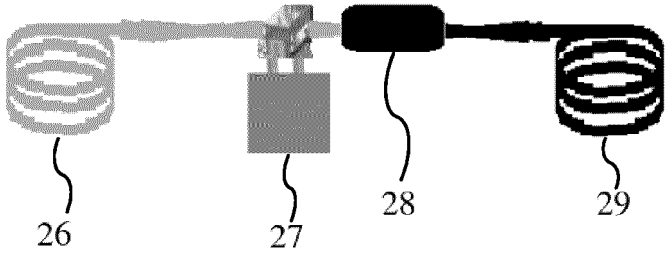

FIG. 6

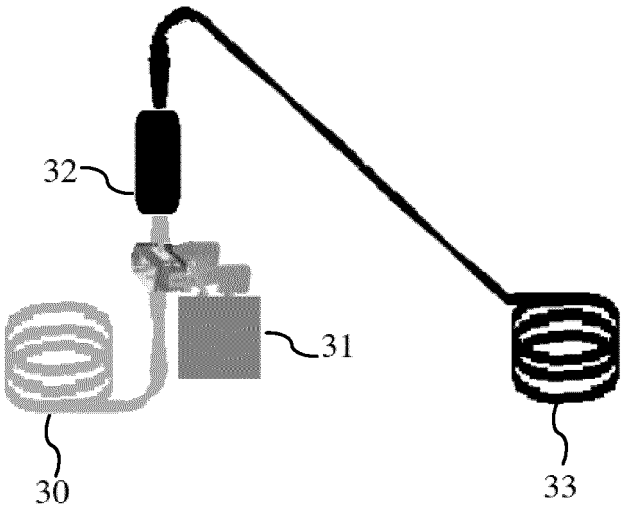

FIG. 7

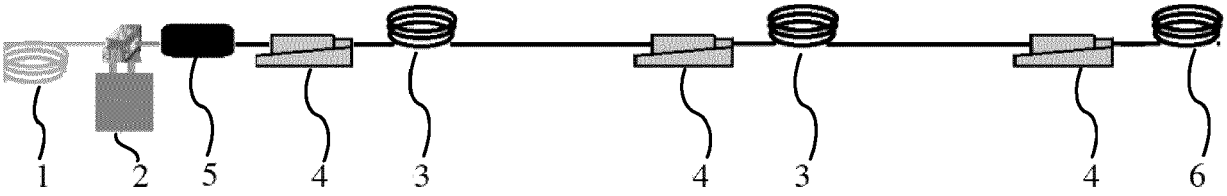

FIG. 8

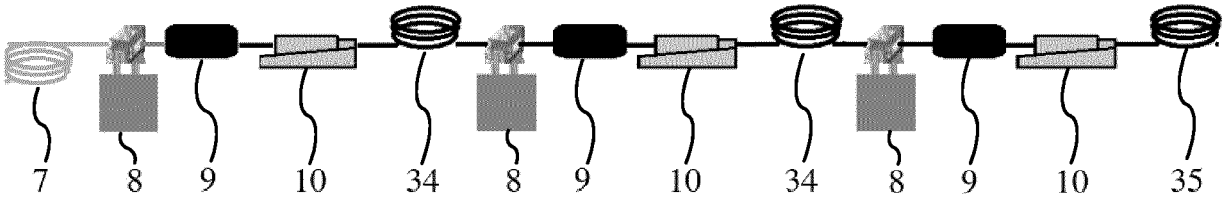

FIG. 9

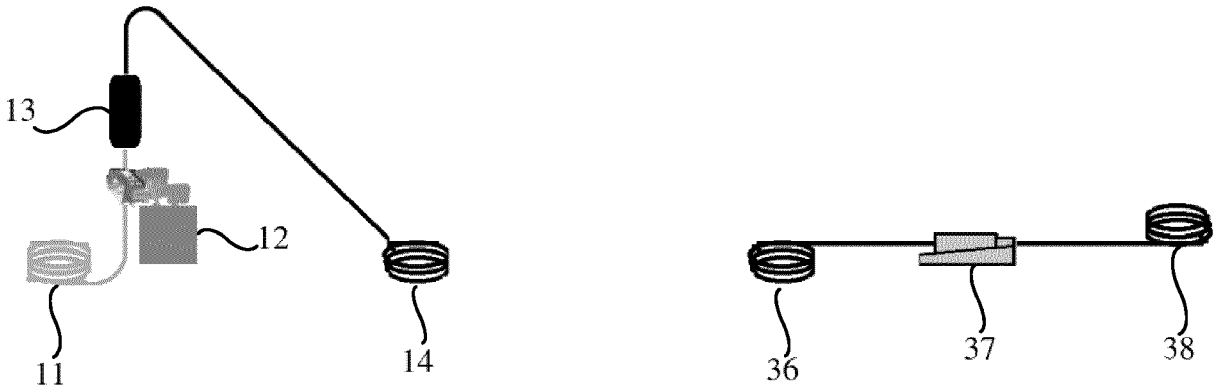

FIG. 10

FIG. 11

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EUROPEAN SEARCH REPORT

Application Number
EP 19 16 8246

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2010/112493 A1 (DSM IP ASSETS BV [NL]; JSR CORP [JP] ET AL.) 7 October 2010 (2010-10-07) * claims 1-9 *	1-15	INV. H01B19/04
X	US 2015/368496 A1 (HAWIG YUHSIN [US]) 24 December 2015 (2015-12-24) * claims 16,22,23; figure 1 *	1-15	
X	US 3 813 322 A (VAZIRANI H) 28 May 1974 (1974-05-28) * column 2, lines 7-10; claims 1-8 *	1,2	

TECHNICAL FIELDS SEARCHED (IPC)

H01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	9 September 2019	Lehnert, Andreas

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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