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

(19) World Intellectual Property Organization
International Bureau

PCT

(43) International Publication Date
12 April 2007 (12.04.2007)

(10) International Publication Number
WO 2007/039098 A2

(51) International Patent Classification:
C23F 13/10 (2006.01)

(21) International Application Number:
PCT/EP2006/009097

(22) International Filing Date:
19 September 2006 (19.09.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
MI2005A001738 20 September 2005 (20.09.2005) IT

(71) Applicant (*for all designated States except US*): **DE NORA ELETTRODI S.p.A.** [IT/IT]; Via Dei Canzi 1, I-20134 Milano (IT).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **TETTAMANTI, Michele** [IT/IT]; Via Santa Caterina 36, I-22079 Villaguardia (IT). **MOJANA, Corrado** [IT/IT]; Via Campogrande 66, I-22868 Valmadrera (IT). **PEDRINELLI, Giorgio** [IT/IT]; Via Veneto 9/6, I-20068 Peschiera Borromeo (IT).

(74) Agent: **REITSTÖTTER-KINZEBACH**; Reitstötter, Kinzebach & Partner (GbR), Sternwartstrasse 4, 81679 München (DE).

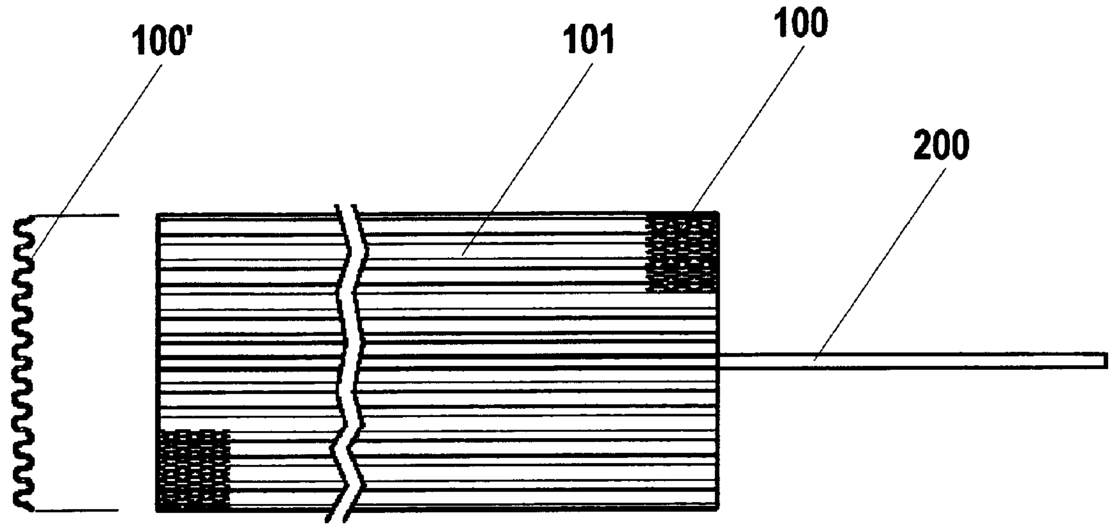
(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DISCRETE ANODE FOR CATHODIC PROTECTION OF REINFORCED CONCRETE



(57) Abstract: It is described a cathodic protection system of reinforced concrete structures with discrete anodes obtained starting from a corrugated planar substrate welded to a longitudinal current collector. The anodes of the invention are particularly suitable for being installed rolled in cylinders, with their axis parallel to the current collectors, positioned inside holes made in the concrete of the structure to be protected.

WO 2007/039098 A2

DISCRETE ANODE FOR CATHODIC PROTECTION OF REINFORCED CONCRETE

DESCRIPTION OF THE INVENTION

The invention relates to the field of cathodic protection of reinforced concrete structures, and in particular to a design of discrete anode for cathodic protection suitable for being installed inside holes or slits made in the concrete.

The corrosion phenomena concerning reinforced concrete structures are known in the art. The steel reinforcement inserted in the concrete structures to improve their mechanical properties normally works in a passivation regime induced by the alkaline environment of the concrete; nevertheless, after a certain time the ion migration across the concrete porous structure provokes a localised attack to the protective passivation film. Particularly worrying is the attack by chlorides, which are virtually present in all kinds of environments where the reinforced concrete structures are employed, and to an even higher extent where an exposure to brackish water (bridges, pillars, buildings located in marine zones), antifreeze salts (bridges and road structures in cold regions) or even seawater, such as for instance in the case of piers and docks, takes place. The critical value of chloride exposure has been estimated around 0.6 kg per cubic metre of concrete, beyond which the passivation state of the reinforcing steel is not guaranteed. Another form of concrete decay is represented by the phenomenon of carbonatation, that is the formation of calcium carbonate by reaction of the lime of the cementitious mixture with atmospheric carbon dioxide. Calcium carbonate lowers the concrete alkali content (from pH 13.5 to pH 9) bringing iron to an unprotected state. The presence of chlorides and the simultaneous carbonatation represent the worst of conditions for the preservation of the reinforcing bar of the structures. The corrosion products of steel are more voluminous than steel itself, and the mechanical stress arising from their formation may lead to concrete delamination and fracturing phenomena, which translate into huge damages from the point of view of economics besides that of safety. For this reason, it is known in the art that the most effective method for indefinitely prolonging the lifetime of reinforced concrete structures exposed to the atmospheric agents, even in the case of remarkable salt concentrations.

consists of cathodically polarising the steel reinforcement. In this way, the latter becomes the site of an oxygen cathodic reduction, suppressing the anodic corrosion and dissolution reactions. Such system, known as cathodic protection of reinforced concrete, is practised by coupling anodic structures of various kinds to the concrete, with the reinforcement to be protected acting as a cathodic counterelectrode; the electrical currents involved supported by an external rectifier travel across the electrolyte consisting of the porous concrete partially soaked with a salty solution. The installation of a cathodic protection system may be carried out since the beginning, on newly constructed structures (in such case, reference is often made to a "cathodic prevention system") or as a retrofitting of older structures.

The anodes commonly used for the cathodic protection of reinforced concrete consist of a titanium substrate coated with transition metal oxides or other types of catalysts for anodic oxygen evolution. As the substrate it is possible to make use of other valve metals, either pure or alloyed; pure titanium is however the largely preferred choice for the sake of cost. From the system design standpoint, the cathodic protection of a reinforcing frame may be carried out according to two distinct ways, that is with distributed or with discrete anodes. The protecting structure with distributed anodes provides covering the concrete cover surface of the reinforcement to be protected, suitably prepared, with anodes consisting of highly expanded meshes; the anodes are then covered with a few centimetre thick fresh cement layer. Alternatively, mesh or solid ribbons can be installed in conduits cut within the cover (whose depth is not sufficient to reach the iron), then filling said conduits with cement mortar. In newly constructed structures finally the anodes, typically anode mesh ribbons, can be installed directly over the reinforcing cage, kept electrically insulated from the iron by means of plastic or concrete-like spacers. The anodic system is embedded in the structure at the time of casting the concrete for the construction. A slight direct current (typically from 1 to 30 mA per m^2 of reinforcement) applied to the anodes, distributed along the whole structure, imposes a uniform cathodic potential to the reinforcement to be protected in case the latter has a sufficiently simple and regular shape. Conversely, if the reinforcement has a complex shape and presents some portions which are less accessible than others, or which have a different steel density per unit surface or other kinds of irregularities, it may be troublesome to ensure a sufficient protection to all of the reinforcement portions without providing an excess of current to other portions. The discrete anode-type protection structure permits to overcome this inconvenience by using separate anodes, for instance in form of bars, plates, rods or segments of mesh or ribbon, installed in suitable holes or slits obtained in the concrete and cemented therein with cement mortar after their placement. The discrete anodes may be placed according to the needs, increasing their number or decreasing their spacing in those spots where it is necessary to provide more current. For some structures finally a combination of mesh and ribbon anodes and of discrete anodes can be provided in order to obtain the best protecting effect. The maximum current density applicable to the above described type of anodes (mesh, ribbons or discrete anodes) is limited by the need of preventing an excessive concrete acidification in the surrounding zone; the latter in fact causes damages of several kinds, among which the build up of reaction products in a limited region around the anode and the consequent mechanical action which deteriorates the surrounding mortar with an inevitable steep rise in the interface resistance. The regulations in force provide a maximum current density per anode effective active surface (that is surface referred to the sum of the two faces) of 110 mA/m^2 at most. Hence, to be able to supply the required protection current in compliance with the maximum current density, it is advisable to maximise the anodic surface per unit length without increasing too much the cost of materials as well as the installation cost associated with the manufacturing of deep holes or cuts in the concrete. Under another aspect, in order to restrict the installation costs it is also necessary to improve the ease of transportation and assembly of the anodes as much as possible. Finally, it is necessary to identify electrode geometries capable of increasing as much as possible the adhesion of the anode to the cement mortar used for their fixing. The electrode geometries of prior art discrete anodes evidence important deficiencies under all of these aspects, for instance because the anode surface increase per unit length may only be achieved by an increase in the diameter or length thereof. Moreover, the installation of cylindrical or of mesh or solid ribbon-shaped anodes may prove very difficult in vertical surfaces or on structure ceilings, wherein such anodes must be suitably anchored to the holes or slits obtained in the concrete before being covered with fresh mortar, to prevent them from falling under the action of gravity.

It is a first object of the present invention to provide a discrete anode for cathodic protection systems of reinforced concrete structures overcoming the drawbacks of the prior art.

In particular, it is one object of the present invention to provide a discrete anode for cathodic protection systems of reinforced concrete structures characterised by high active surface per unit length, ease of transportation, storage and installation, and by high adhesion to the cement mortar.

It is a second object of the present invention to provide a cathodic protection system for reinforced concrete structures of the discrete anode-type.

It is a further object of the present invention to provide a method of installation of a cathodic protection system for reinforced concrete structures of the discrete anode-type.

These and other objects will be clarified by the following description, which has a mere exemplary purpose and does not intend to constitute a limitation of the invention.

The anode of the invention consists of a corrugated titanium or other valve metal planar substrate, welded to a current collector and provided with a superficial catalytic activation, suitable for being rolled on itself in order to form a cylinder.

As it will be evident from the present description, the term cylinder is hereby used to generally encompass surfaces generally approximating a cylindrical shape, in particular disregarding the deviation introduced by the corrugations.

The corrugated substrate preferably consists of a thin undulated mesh, and the current collector is preferably a rod or strip, for instance welded to the centre or along one side of the activated substrate.

The term corrugated substrate is hereby used to generally refer to a substrate having a profile formed into folds or furrows of any shape suitable to define a grooved surface, including folds with a continuous bend and pleats with sharp corners optionally in combination with flattened ends.

The substrate must be thin enough to be easily subjected to the cylindrical folding, which is preferably carried out parallel to the main dimension of the current collector; the substrate thickness must on the other hand be sufficient to maintain a permanent superficial corrugation, and to impart an elastic behaviour to the cylindrically folded anode. In one preferred embodiment, the substrate is an undulated mesh of initial thickness comprised between 0.2 and 2 mm, length comprised between 30 and 300 mm, with a number of grooves per linear metre comprised between 20 and 2000. The final thickness after the corrugation process which defines the grooved geometry is preferably comprised between 1 and 30 mm. The cathodic protection system of the invention comprises a multiplicity of anodes of the invention folded into cylinders, forcedly inserted in suitable cylindrical holes or openings made in suitable zones of the concrete surrounding the metallic reinforcement to be protected and fixed with cement mortar. The anodes of the cathodic protection system of the invention may be further provided with an external insulating ring or other equivalent means to prevent short-circuiting with the surrounding exposed rebar, as known in the art. As an alternative, the anode may be pre-filled with cement mortar or other porous electrically insulating material before its insertion in the appropriate hole. According to a further embodiment, the anode can be pre-welded in a cylinder before installation in the concrete. This configuration is particularly preferred when the drilling of the relevant hole is liable to cut across the reinforcing bars and the installation of an anode in form of open cylinder could cause a short circuit between the anode cylinders and the reinforcing bar exposed by the drilling procedure. A pre-welded cylindrical anode can be suitably used when cathodic prevention is applied during construction of a concrete structure. Such preformed cylinders can be installed on the rebar cages suitably distanced by an insulating spacer. In particular, the anode cylinder can be precisely positioned near the high steel density areas of the rebar cage in order to assure an optimum localised current distribution. The anode of the invention may be also installed without a cylindrical folding, that is in a flat or intermediate bent open position (e.g. folded in a semicircle or crescent and the like), in suitable slits made in the concrete. The advantages of this type of construction will be apparent to one skilled in the art: the corrugated substrate presents a much bigger active surface than the projected surface (for instance 1.5 times as much or more), so that the total current which can be supplied in compliance with the regulations per unit length is increased by a significant factor, preferably by 50% or more. The anodes are easy to activate

and transport, since they can be catalyst-coated and handled as planar sheets, and effortlessly folded into cylinders at the time of their use; the current collector may be fixed before or after the transportation according to the needs. The anode, manually folded and optionally kept in a cylindrical shape by application of clips, is forced into the holes made in the concrete, optionally by aid of a guide tube of plastic material subsequently extracted from the site. The elastic behaviour of the anode contributes to a good fixing to the walls of such holes; the anchoring of the cement mortar, subsequently cast or sprayed into the holes at the moment of fixing and optionally also applied to the anodes prior to their insertion in the holes, is favoured by the anode corrugated surface.
For the sake of a better understanding of the invention reference will be made to the following drawings, having the purpose of illustrating some preferred embodiments thereof without constituting any limitation whatsoever.

- Figure 1 presents a plan view and a cross-section of a first embodiment of the anode of the invention.
- Figure 2 is a plan view of a second embodiment of the anode of the invention.
- Figure 3 shows a detail of the fixing of the undulated substrate of the anode of Figure 1 to the current collector.
- Figure 4 is a top-view of the discrete anode of the invention installed in the relevant cathodic protection system of reinforced concrete structures.

In detail, figure 1 shows a plan view of the anode of the invention manufactured on a planar substrate which in the specific case is an undulated mesh (100); for the sake of clarity of the drawing, the undulated mesh corrugation was identified as (101) in a schematic fashion, without reproducing the surface design thereof. (100') indicates the cross section of the same undulated mesh. The undulated mesh is just one of the possible corrugated substrates enabling to practise the invention, but many other geometries can be fit to the scope including among others solid, perforated or expanded sheets, metal foams and the various combinations obtainable by juxtaposing solid or preferably foraminous elements of such kind; decisive factors for the choice of a particular corrugated substrate geometry are given by the ease of folding into cylinders, by the elastic behaviour and by the ease of obtaining and maintaining a permanent corrugation. The anodic substrate (100) is activated by means of a catalytic coating known to those skilled in the art, preferably containing catalysts for oxygen evolution reaction, for example mixtures of noble metals such as iridium, platinum, palladium, ruthenium, oxides thereof and/or oxides of other transition metals such as titanium, tantalum, niobium, zirconium, molybdenum, cobalt and others. In the embodiment of figure 1, a current collector (200) is welded to the corrugated substrate (100) in a central position; such current collector is in this case a rod, but it may also consist of a bar or strap or other longitudinal current collector known in the art.

Figure 2 shows a plan view of an embodiment of the anode of the invention equivalent to that of figure 1, except for the current collector (200) being welded in a lateral position with respect to the planar substrate (100). In both cases, the invention provides the planar substrate to be preferably folded by joining the two parallel edges to the current collector so as to form a cylinder at the time of installation.

In figure 3 there is shown a detail of the fixing of the undulates mesh acting as the anodic substrate (100) to the current collecting rod (200) by means of a weld (300) executed in accordance with one of the techniques known in the art.

Figure 4 shows a top-view of the discrete anode of the invention installed in a cathodic protection system for reinforced concrete structures; the corrugated substrate (100) is rolled in a cylinder with axis parallel to the current collector (200) and the anode is forcedly inserted into a hole (400) obtained in the concrete (500). After the installation, the anode is fixed by a cement mortar application (not shown). A multiplicity of anodes installed according to an equivalent embodiment, distributed in accordance with the protection requirements of the steel reinforcement and anodically polarised, constitutes the cathodic protection system of the discrete anode-type of the invention. The corrugated substrate (100) as displayed in figure 4 has a profile with continuous bends, however it will be obvious to one skilled in the art that the invention may be practised with other types of corrugated substrates without departing from the scope thereof, for instance with a pleated substrate having sharp corners, whose top-view results in a star-type profile once rolled in a cylinder.

EXAMPLE

A 0.6 mm thick narrow-mesh net of 5 m² size was activated with a noble metal catalytic coating suitable for working in the concrete, and subsequently corrugated and cut in several 150 mm wide and 200 or 400 mm long pieces. The anodes so obtained have a current capacity of respectively 6.7 or 13 mA at a maximum current density of 110 A/m². Such current supply represents a higher value compared to prior art anodes for a given applied current density. A titanium rod was spot-welded in a central position as the current collector to each of the pieces obtained. The thus formed anodes were brought to a construction site wherein a cathodic protection system had to be installed for the ceiling and the columns of a bridge, particularly contaminated by chlorides in the water discharge zones from the overlaying road pavement. These zones required a particularly high current localised in the most contaminated portions (anodic zone).

250 mm deep and 65 or 130 mm wide holes, spaced by about 500 mm, were made in the concrete of the ceiling and of the columns, for easily installing the anodes of the present invention in their interior, suitably rolled in cylinders by hand. To facilitate the installation in the pillar walls, plastic guide tubes were inserted in the holes obtained in the concrete, their diameter being slightly lower than that of the hole. The cylindrically-folded anodes were inserted inside the guide tube. At the time of positioning each anode, the guide tubes were removed. The anodes thus remained perfectly anchored to the wall of the hole allowing an easy filling of the latter by the operator. To install the anodes in the ceiling, they were formed in cylinders and the cylindrical shape was stabilised by using metal or plastic clips permitting a sufficient elastic allowance of the cylinder itself. Also in this case, once installed inside the holes of the ceiling to be protected, the cylindrical anodes were perfectly anchored to the internal surface of the holes themselves. In other areas of the bridge to be protected, more easily accessible, the anodes could be installed after being manually rolled in cylinders, with no need for guide tubes or for metal or plastic clips. After the installation, the anodes were suitably connected to a current rectifier by an appropriate wiring. Silver/silver

chloride reference electrodes were also installed for monitoring the protection level.

The cathodic protection system was activated for a period of about 30 days after which the 100 mV depolarisation test, as universally prescribed by the norms for measuring the correct functioning of the system, was successfully performed.

The previous description is not intended to limit the invention, which may be used according to different embodiments without departing from the scopes thereof, and whose extent is univocally defined by the appended claims.

Throughout the description and claims of the present application, the term "comprise" and variations thereof such as "comprising" and "comprises" are not intended to exclude the presence of other elements or additives.

CLAIMS

1. Anode for cathodic protection comprising a corrugated metal planar substrate welded to a current collector.

2. The anode of claim 1 wherein said metal planar substrate consists of a valve metal coated with a catalytic active layer.

3. The anode of claim 2 wherein said valve metal is pure titanium.

4. The anode of any one of claims 2 or 3 wherein said catalytic active layer comprises noble metals and/or oxides thereof and/or oxides of other transition metals.

5. The anode of claim 1 wherein said metal planar substrate is selected from the group of meshes, solid, perforated or expanded sheets, metal foams, juxtapositions of meshes, sheets or foams.

6. The anode of claim 5 wherein said metal planar substrate is a mesh of initial thickness comprised between 0.2 and 2 mm, and of final thickness after corrugation of 1 to 30 mm.

7. The anode of claim 5, wherein the corrugation of said metal planar substrate defines a number of grooves comprised between 20 and 2000 per linear metre.

8. The anode of any one of the previous claims wherein said current collector is a metal rod, bar or strap.

9. The anode of any one of the previous claims pre-welded in a cylindrical shape.

10. The anode of any one of the previous claims further provided with an external ring or equivalent insulating means.

11. Cathodic protection system of reinforced concrete structure consisting of a metal reinforcement embedded in concrete, comprising a multiplicity of anodes of any one of the previous claims rolled in open cylinders having the axis parallel to said current collector, forcedly housed in a multiplicity of holes obtained in the concrete.

12. Cathodic protection system of reinforced concrete structure consisting of a metal reinforcement embedded in concrete, comprising a multiplicity of anodes of any one of the previous claims forcedly housed in a flat or bent open position in a multiplicity of slits drilled in the concrete.

13. The cathodic protection system of claim 11 or 12 wherein said anodes are embedded in the concrete inside said holes or said slits by application of a cement mortar.

14. Method for the installation of a cathodic protection system in a reinforced concrete structure consisting of a metal reinforcement embedded in concrete, comprising obtaining a multiplicity of holes in the concrete, forcedly housing inside each of said holes an anode of any one of claims 1 to 10 folded in a cylindrical position with axis parallel to said current collector and fixing said anodes inside said holes with cement mortar applied by casting or by spraying.

15. Method for the installation of a cathodic protection system in a reinforced concrete structure consisting of a metal reinforcement embedded in concrete, comprising obtaining a multiplicity of holes in the concrete, forcedly housing inside each of said holes a stiff plastic guide tube, inserting in each of said tubes an anode of any one of claims 1 to 10 folded in a cylindrical position with axis parallel to said current collector, extracting said guide tubes leaving behind said anodes and fixing said anodes inside said holes with cement mortar applied by casting or by spraying.

16. The method of any one of claims 14 or 15 wherein said folded anodes are stabilised in the cylindrical position by metal or plastic clips.

17. The method of any one of claims 14 to 16 wherein prior to said forced housing of said anodes inside said holes, each of said anodes is pre-filled with a porous electrically insulating material, optionally cement mortar.

18. Method for the cathodic protection of a reinforced concrete structure consisting of applying an anodic potential to said anodes of said cathodic protection system of any one of claims 11 to 13.

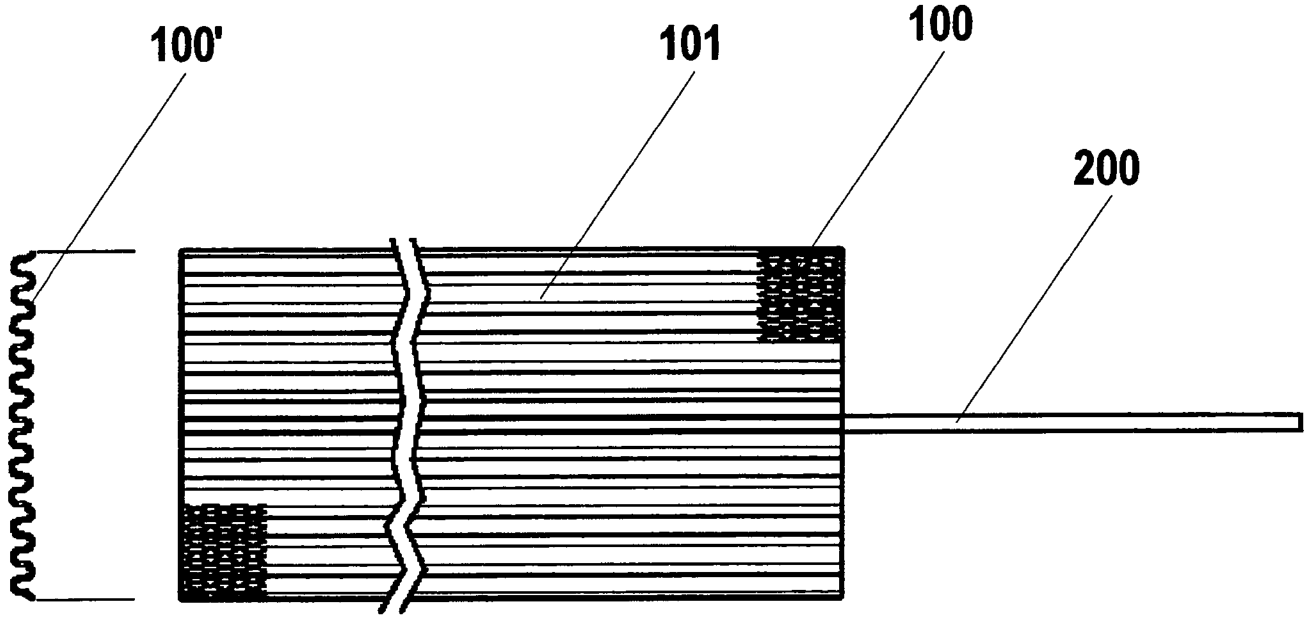


fig. 1

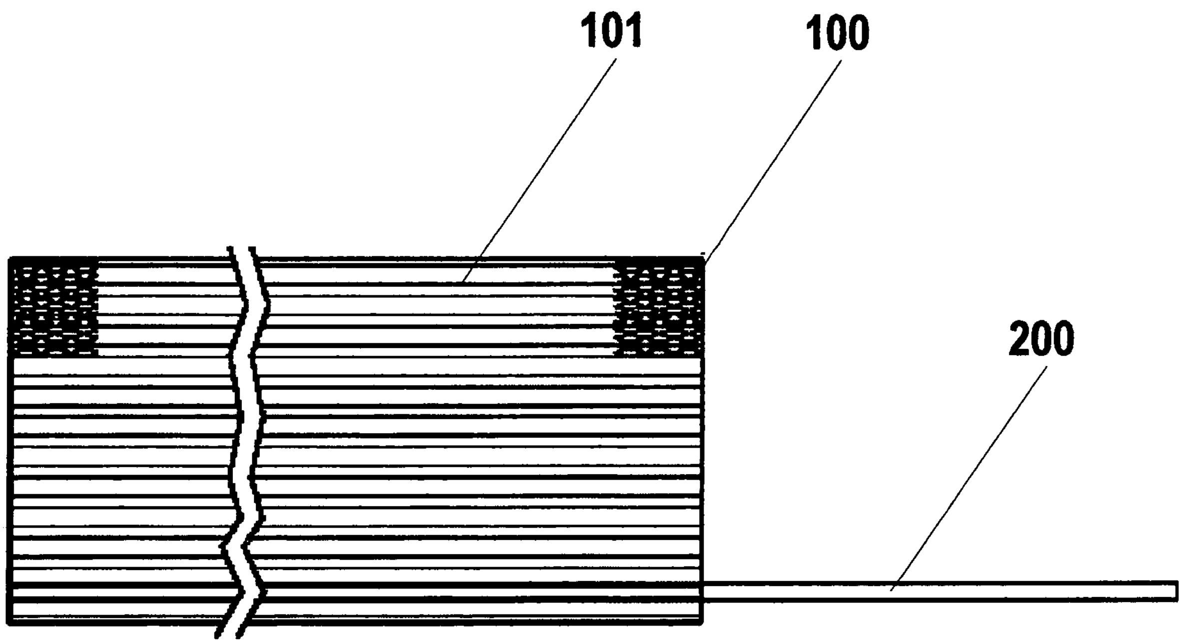


fig. 2

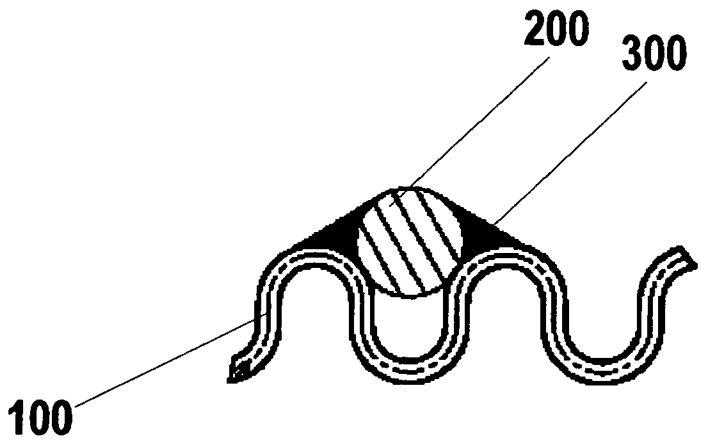


fig. 3

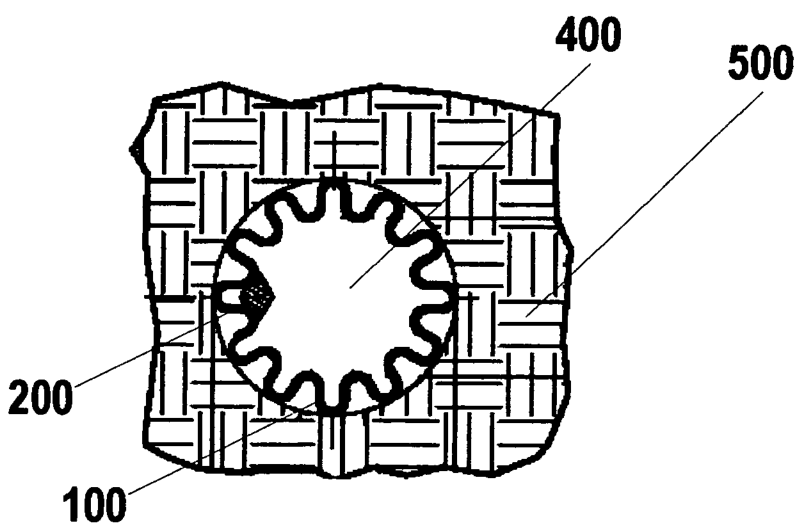


fig. 4