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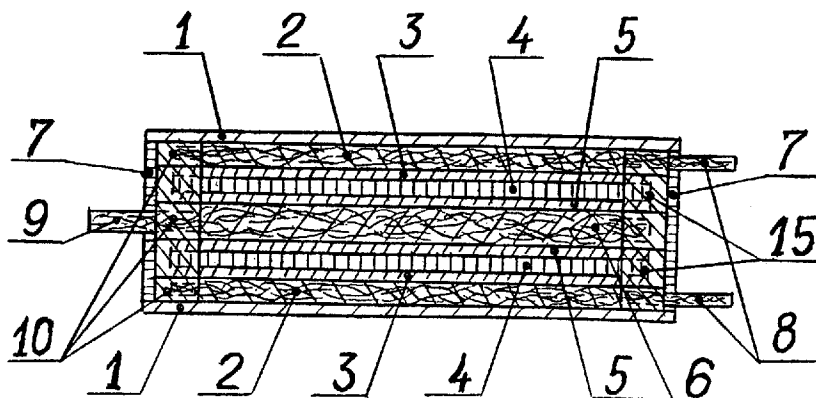
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(54) **ACCUMULATEURS A GRANDE CAPACITE ENERGETIQUE**

(54) **HIGH POWER CAPACITY ACCUMULATORS**



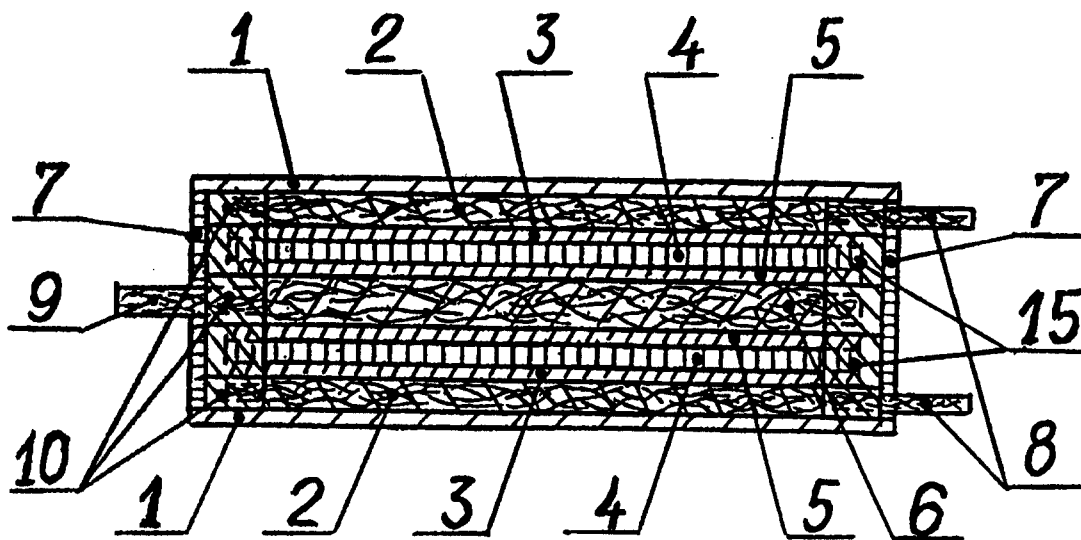
(57) L'invention concerne un accumulateur fabriqué selon le procédé suivant: on dispose les différents éléments - électrodes positive et négative, électrolytes des films/membranes, séparateurs - le long du périmètre à l'intérieur des cadres, et on les incorpore dans des films ou des couches constitués d'un matériau thermoplastique inerte; on assemble les cadres par collage ou soudage, avec une technique appropriée, dans une zone de soudure spéciale; on soude sur les cadres des films ou des couches de protection appropriés, tandis qu'on amène les sorties de contact des électrodes aux emplacements désirés en les faisant passer au travers des cadres.

(57) Accumulator, the elements of which - the positive and negative electrodes, films/membranes electrolytes, separators are worked along the perimeter into the frames and mutually included in inert thermoplastic material films or sheets, gluing or welding the frames together with any suitable method, in a special welding area, cover films or sheets are welded to them, whereas the contact outlets of the electrodes in required places are brought through the electrode frames, is being proposed.

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(21) International Application Number: PCT/LV97/00001 (22) International Filing Date: 7 March 1997 (07.03.97) (30) Priority Data: P-96-450 5 December 1996 (05.12.96) LV (71) Applicant (for all designated States except US): SPRI- NOVSKIS, Janis [LV/LV]; Elizabetes Street 2-1a, LV-1010 Riga (LV). (71)(72) Applicant and Inventor: BAUZE, Aivars [LV/LV]; Sil- ciema Street 15/3-48, LV-1024 Riga (LV). (74) Agent: FOGEL, Abraham; Alfa-Patents, Marstalu Street 2/4, LV-1050 Riga (LV).		(81) Designated States: AU, CA, CN, JP, KR, UA, US, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>With amended claims.</i>

(54) Title: HIGH POWER CAPACITY ACCUMULATORS**(57) Abstract**

Accumulator, the elements of which – the positive and negative electrodes, films/membranes electrolytes, separators are worked along the perimeter into the frames and mutually included in inert thermoplastic material films or sheets, gluing or welding the frames together with any suitable method, in a special welding area, cover films or sheets are welded to them, whereas the contact outlets of the electrodes in required places are brought through the electrode frames, is being proposed.

High power capacity accumulators

1. Description of the invention

The invention "High Power Capacity Accumulator" is related to the second type electrochemical electricity sources.

All presently manufactured and developed accumulators are characterized in the book "Electrochemical energetics", written by N.V.Korovin.

The most widely manufactured and applied are lead, nickel-cadmium, nickel-iron and nickel-zinc accumulators. Chemical compounds of the 4, 5 and 6 periods of the periodical system of elements are being applied as the active substances in the abovementioned accumulators for electrodes, thus the accumulators are heavy, with low power capacity per a mass unit - from 10 to 45 W.h/kg, only the nickel-zinc ones - from 50 to 70 W.h/kg. The voltage between the electrodes of one cell is not high either - from 1 to 2 V. The active substance participates in the electrochemical reaction of charging and discharging processes with one or two electrons, apart from that often also the components of the electrolyte participate in those chemical reactions. The work resource of the accumulators is not very large - from a few hundred to a few thousand cycles, for example, for power capacity nickel-zinc accumulator - from 100 to 400 cycles.

More energy intensive are nickel-hydrogen, bromine-zinc accumulators - from 40 to 75 W.h/kg, and chlorine-zinc ones - even from 100 to 150 W.h/kg. But they also have some of the above mentioned drawbacks - not a very high voltage between electrodes of one cell - from 1,1 to 1,95 V, and a small operative resource - from 200 to 1500 cycles, exception being the nickel-hydrogen accumulator, the operative resource of which is high - from 2000 to 10000 cycles. A significant drawback of these accumulators is the great self-discharge speed, which can reach even several per cents per hour, the high energy capacity chlorine-zinc accumulators possess the greatest self-

discharge speed. There are problems with storage of hydrogen and halogens in the accumulator, the storage of chlorine is especially difficult and complicated. The problems are caused also by the high diffusion capacity of these substances, which initiate and intensify self-discharge of accumulator. As to fire safety, the leaks of hydrogen are dangerous, but chlorine and bromine in the case of a leak can cause serious contamination of the environment and even threaten human lives.

Sulfur-sodium accumulators and lithium accumulators where the non-aqueous electrolytes have been applied have the highest power capacity.

A significant drawback of sulfur-sodium accumulators is their high working temperature - from 150 to 300°C, the power capacity is high - from 70 to 230 W.h/kg; the voltage between the electrodes of one cell - from 1,75 to 1,85 V; the working resource - from 1000 to 5000 cycles.

The power capacity of lithium accumulators with non-aqueous electrolyte is from 60 to 200 W.h/kg; the voltage between the electrodes of the same cell can be from 1,5 to 3 V. The electrolyte components participate in the charging/discharging chemical reaction. The operation of these accumulators is unstable, dendrite growth progresses and the electrode passivates; their working resource is also low - from 100 to several hundred cycles. The working temperature of many of them can be from 50 to 150°C and their properties deteriorate to a great extent, if the temperature is below 25°C. If the stability of the accumulator and the working resource are increased up to even 1000 cycles, and the work regime is perfected, the power capacity decreases several times.

The active substance of the accumulator often is of low conductivity, to increase it special components are added to the active substance or/and collectors, contact outlets of the current are made of metal, but thus the power capacity of the accumulators is reduced. Often the thin layer of the active substance of the electrode directly contacting with the electrolyte takes part in the electrochemical process, at the same time the active substance increases passivity and as the result, the power capacity of the accumulator is reduced, because the active substance is not used to full extent. In the course of operation the energy storage capacity can decrease very significantly.

A rapid self-discharge, caused by the high mobility/diffusion of the atoms of the active substance, takes place in the accumulators of high power capacity, where hydrogen or halogens (chlorine, bromine) are being applied as active substances. Also gas storage in the accumulator is problematic, apart from that these active substances are dangerous, if a leakage occurs.

As to the charge/discharge process of many accumulators the electrolyte components participate directly in the electrochemical reactions, thus during the processes the properties and the working parameters of the electrolyte alter, as a result the quality of the active substance of electrodes deteriorates - its structure changes, passivates, dendrites develop. All that deteriorates the operating parameters of the accumulator, that is, decreases the time of service, the work resource, as a result constant monitoring and qualified servicing is necessary during operation.

Expensive and scarce materials are often being used for the accumulators.

Creating chains and parallel connections of accumulator cells, usually their weight and volume, are being increased, as a result their total power capacity is being reduced.

The aim of the invention is to increase as much as possible the total power capacity of the accumulator, battery of cells in parallel or/and chain switching per one weight and capacity unit; to ensure their stable, long-term operation and energy storage with minimal losses (minimal self-discharge); to achieve the possible minimal monitoring and simple servicing; to provide the opportunity to develop both small and theoretically infinitely large accumulators (chains of cell batteries and parallel connections); to guarantee safe usage of these high power capacity accumulators in such a way that they would be harmless for the humans and environment.

For fastening together and packing the accumulator elements (to create an enclosure) the prior art is Patent WO 86/03060, where the elements of the accumulator together with the electrolyte are enclosed leak-tight in relation to the electrodes and electrolyte in inert thermoplastic material films or sheets, which are welded along the perimeter in a special area by the method of thermal compression. The contact outlets/collectors are hermetically taken through the welded area.

In the invention submitted herein (Fig. 3, 4 and 5) the electrodes (2, 6) and film/membrane - electrolyte (4), which from both sides is covered by separators (3, 5), have been worked in along the perimeter in relation to electrodes and electrolytes into inert thermoplastic or other suitable material frames (10). Minus (2) and plus (6) electrodes contact outlets/collectors (8, 9) are hermetically taken through the material of the frames.

The electrodes (2, 6) and separators (3, 5) are being filled/saturated with a corresponding electrolyte and arranged into a definite order (Fig. 1, 2 and 9), from both sides covered with a thermoplastic or other suitable material films or sheets, inert in

relation to electrodes and electrolytes (1). If necessary, when creating cell connections (Fig. 10), films or sheets (1) isolate also elements or their blocs of the adjacent cells (20). Afterwards the frames (10, 15), into which the respective elements of the accumulator have been worked in, and the covering/separating films or sheets (1), arranged in a definite order (Fig. 7 and 8), are being fastened together by welding or gluing, forming the welded or glued seam (17) with any method appropriate in each case. If necessary (Fig. 8) a special layer is being welded over or overlaid/formed (7).

Contrary to the prior art, in the submitted invention as described herein, compact, small, as well as theoretically infinitely large accumulators and different connections of cells with high power capacity can be formed. The variety and opportunities for choosing materials, applicable for enclosing the accumulator and separating the elements or blocks of cells increase, for fastening any most feasible, appropriate and effective gluing or welding methods and means, as well as their combinations can be used. As a result better quality of the covering/packing, sealing, endurance and safety can be reached, enlarging the weight to a very small extent only.

For applying frames, formed along their perimeter to fasten together the elements of the accumulator and to separate them the prior art is to be found in patent EP 0558755 where the frame is made from thermoplastic electroisolating material and separates the minus electrode from the plus electrode, as well as serves for mechanical fastening of both electrodes and ensuring of their sealing. The contact outlets/collectors of the electrodes are positioned and fitted to both sides of the frame.

In the invention applied for herein (Fig. 3, 4 and 6) the frames of the elements of the accumulator are part of their design, elements - electrodes (2, 6) and film/membrane - electrolyte (4) with separators (3, 5) have been worked into the material (10, 15) of the frames and the required places (11) through the material of electrode frames contact outlets/collectors have been taken (8, 9). The frames of the electrodes completely or in part can be manufactured of electroconductive material, thus increasing the parameters of accumulator operation. It is possible to do this, because, when arranging the elements of the accumulator (Fig. 1, 2, 7, 8 and 9), the frames of the electrodes (10) are interspersed by electroisolating material films/membranes, namely, frames (15) of electrolyte with separators, or by (Fig. 10) separating films or sheets (1). The frames (10, 15) have been fastened together (Fig. 7 and 8) and by covering/separating films (1), forming seams (17). When necessary (Fig.

8), to increase the endurance, sealing and safety of the cover/packing construction, a special layer is being formed (7).

To separate the plus electrode from the minus electrode and guarantee, that they do not touch and form a direct electrical contact, the patent WO 90/13924 has been applied, where between the plus and minus electrodes a separator of a suitable material, inert in relation to the electrodes and electrolyte, has been placed.

In the invention submitted herein (Fig. 6) two thin separators are placed between the minus and plus electrodes (3, 5) and a membrane/film-electrolyte (4) is installed between them. The material of the respective separators (3, 5) is inert in relation to the electrodes (2, 6) and the electrolytes, the material of the minus electrode side separator (3) can be different from the plus electrode side separator (4) material. Such positioning (3, 5) of separators (Fig. 1 and 2) guarantees, that the film/membrane-electrolyte would not be mechanically damaged and will not touch directly with the electrodes (2, 6), the electrodes will not affect it. Thus a higher stability, safety and higher work resource of accumulator operation is ensured, especially with high voltage between the electrodes of the same cell. It is easier to find, apply the most suitable material from the range for the separators (3, 5).

Example 1

The cells of the accumulator (Fig. 1) consist of the elements: two minus electrodes (2), between which a plus electrode (6) is positioned, all electrodes each separately, have been worked into frames (10) and brought out through the material of the frame into a definite area (11), the contact outlets/collectors (accordingly 8, 9); minus and plus electrodes (2, 6) have been separated by two thin separators (3, 5 accordingly) between them a film/membrane-electrolyte is positioned (4) and they have been worked into a frame (15). The essence does not change, if according to the need the positions of minus and plus electrodes (2, 6) and accordingly also separators (3, 5) are mutually interchanged.

The electrodes (2, 6) and the respective separators (3, 5) are filled/saturated with an electrolyte of a appropriate composition and all elements together with the electrolyte are arranged in a definite order. They are from both sides covered with films/sheets (1) of a fitting/respective material and fixed together, welding or gluing the frames of the elements (10, 15) and films or sheets (1) with any suitable/feasible

method. When necessary for assuring required properties, a special layer is being formed (7).

According to the method, described in this example, accumulators, parallel cell battery connections with theoretically infinitely large number of elements (Fig. 9) can be formed, accordingly supplementing the number of electrodes (2, 6) and separators, between which a film/membrane-electrolyte (16) is positioned, and arranging them into a definite order. Thus high power capacity accumulators can be obtained with theoretically unlimited power capacity and one cell voltage between the current outlets.

Example 2

The cell of the accumulator (Fig. 2) consists of a minus electrode (2), a plus electrode (6), separated by two thin separators (3, 5) accordingly, between which a film/membrane-electrolyte has been positioned (4). All elements have been worked into frames (10, 15 accordingly). Electrodes (2, 6) and the corresponding separators (3, 5) are accordingly filled/saturated with an electrolyte of a corresponding composition and all elements together with the electrolyte are arranged in the determined order. Both sides of them are covered with films/sheets (1) of a corresponding/suitable material and everything is fixed together, welding or gluing the frames of the elements (10, 15) and films or sheets (1) with any suitable/feasible method.

According to the method, described in this example, thin, theoretically infinitely large accumulators can be formed. They can be flexible enough, to be formed into a spiral or positioned inside the case or other suitable/feasible cover. To increase the voltage of the battery of the accumulator the necessary number of cells can be switched into a chain connection.

Example 3.

To obtain accumulators with required power capacity and voltage with a high power capacity per unit of weight and volume, they (Fig. 10) are formed from cells or cell battery parallel connection blocs (20), positioning between them the separating films or sheets (1). Both sides of the properly arranged packing are covered with sheets or films (1), all elements and separating/covering films or sheets are fixed together,

welding or gluing the frames of the elements into a bloc (21) with any suitable/feasible method. In case of necessity, to yield the required properties, a special layer (7) is being formed, if necessary the contact outlets/collectors of the electrodes (8, 9) and the areas of their connection can be placed into this layer.

High power capacity accumulators, various cell battery connections with theoretically unlimited power capacity and voltage can be formed, they can be applied when necessary.

The prior art of the contact outlets/collectors of the carbon electrodes is patent EP 04190090, where the carbon minus electrode consists of two layers. One layer ensures the charge/discharge process, but the other layer executes the function of the contact outlet/collector. The second layer contains metals of the iron group to increase the electroconductivity. In the invention, submitted herein (Fig. 3, 4, 5) the active substance of the minus and plus electrodes (2, 6) contains throughout chemical and mechanical graphite compounds with metal, which serves simultaneously as the active substance to ensure charge/discharge processes and to increase the electroconductivity of electrodes. The outlets/collectors of the electrodes, which go through the material of the frame (11), as well as outside the frame (8, 9), to increase electrical conductivity contain throughout chemical and mechanical graphite compounds with metal. In this compound there can be metals of iron group and/or the same metals, which are present in the active substance of the electrode:

- the alkaline or alkaline earth metals, magnesium and aluminum for minus electrode;
- transition group metals, such as iron group metals, or chromium or manganese for plus electrode.

The carbon-graphite long-fiber contact outlets/collectors (8, 9, 11), containing chemical and mechanical graphite compounds with metal are in the form of cardboard, felt or woven material.

For each specific carbon minus and plus electrode the material of carbon - graphite long-fiber contact outlets/collectors (8, 9, 11), may contain specific metal or - several metals to increase electrical conductivity.

The prior art for the active substance of carbon electrodes is patent JP 60-20466, where long-fiber carbon-graphite material, containing a chemical compound of graphite with nickel has been applied for a high power capacity accumulator.

In the invention submitted herein (Fig. 3, 4, 5) carbon-graphite long-fiber material (13) or carbon-graphite long-fiber material in composition with high graphite content carbon component (12) for the active substance of carbon plus and minus electrode (2, 6) for a high power capacity accumulator has been used, the long-fiber material (13) and the high graphite content carbon component (12) contains chemical or mechanical compound with metal.

The chemical or mechanical compound contains:

the alkaline or alkaline earth metals or magnesium and aluminum for the active substance of the minus electrode;

transition group metals, such as iron group metals, chromium or manganese for the active substance of the plus electrode.

In the patent JP 60-23963 the carbon-graphite long-fiber material in the form of cardboard or felt has been used for the active substance of the plus electrode and it is the prior art of the invention submitted herein.

In the invention submitted herein (Fig. 3, 4, 5) cardboard, felt or woven material of carbon-graphite fiber (13) has been applied as the active substance for carbon plus and minus electrodes. The active substance of the carbon electrode (Fig. 3) may consist only of carbon-graphite long-fiber material (13) or a composition (Fig. 4, 5) of carbon-graphite long-fiber material with a high graphite content compound (12).

The prior art of the structure for the active substance of the carbon electrode is the patent WO 90/13924, where the composition of the active component of the carbon minus electrode consists of a high graphite content carbon component and short-fiber carbon component - soot.

In the invention submitted herein (Fig. 4, 5) the composition of the active substance of the carbon minus and plus electrode (2, 6) consists of a high graphite content carbon component (12) and carbon-graphite long-fiber component (13), which can be felt, cardboard or woven material. The high graphite content component (12) (Fig. 4) has been worked into carbon-graphite long-fiber (13) felt or cardboard, as well as the high graphite content carbon component (12) can be placed in a layer (Fig. 5) between the carbon-graphite long-fiber (13) felt, cardboard or woven material.

Example 4 (Fig. 3)

The carbon plus and minus electrodes (6, 2) consist of carbon-graphite long-fiber cardboard, felt or woven material. There may be one or several layers of the carbon-graphite long-fiber material. The material, applied in the layers, may be of identical structure or, if it is necessary to ensure specific properties, the material, applied in the layers, may be of a different structure: cardboard, felt or woven material.

The material of the electrode along the perimeter (11) has been worked into a frame (10). In the appropriate spot (11) the carbon-graphite long-fiber contact outlets/collectors of the electrodes have been laid through the material of the frame. The carbon long-fiber material contains a chemical or mechanical compound with the required metal.

Example 5 (Fig. 4)

The composition of the carbon plus and minus electrodes (6, 2) is formed from two materials of different structure: a high graphite content component (12) and carbon-graphite long-fiber component (13). The high graphite content carbon component (12) has been irregularly worked into the carbon-graphite long-fiber (13) felt and cardboard. The long-fiber component of the electrodes (6, 2) has been worked into the frames (10) along the perimeter (11). In a specific place (11) the carbon-graphite long-fiber material has been laid through the material of the frames and outside the frame (10) and it forms the contact outlets/collectors (9, 8) of the electrodes.

Both components of the active substance of the carbon electrodes and the contact outlets/collectors contain chemical or mechanical graphite compound with the required metal.

Example 6. (Fig. 5.)

The composition of the carbon plus and minus electrodes (6, 2) is formed from two materials of different structure: a high graphite content component (12) and carbon-graphite long-fiber component (13). The high graphite content carbon component (12) has been placed in a layer between the layers of carbon-graphite long-fiber (13) component. The carbon-graphite long-fiber component can be of material with a diverse structure: felt, cardboard or woven material, as well as their composition. The number of the layers of the high graphite content component (12) in the electrodes depends on the envisaged, necessary properties of the accumulator. The long-fiber component (6,

2) of the electrodes has been worked into the frame (10) along the perimeter (11). In the required places (11) through the material of the frame the contact outlets/collectors (9, 8) of the electrodes have been laid.

Both components of the active substance of the carbon electrodes contain chemical or mechanical compound with the required metal.

The prior art for the active substance of the minus electrode of the high power capacity accumulator is the patent WO 90/13924, where the active substance of the carbon electrode is a composition of carbon materials of a diverse structure and all components of the carbon material contain a chemical compound of graphite with a alkali metal. In the patent the compound with lithium has been described. The metal in the compound is not tightly fixed and during the charge/discharge processes the transfer of lithium from the minus electrode to the electrolyte and further to the plus electrode takes place.

The process requires at least room temperature for lithium but in cases when other alkali metals are applied the temperature is to be even higher; it may result in the passivation of the electrodes, the growth of dendrites, deterioration of the required properties of electrode - all this taking place on an accelerated rate. The potential of electrode during discharge is not high either - approximately 1 V whereas at least 3 V are required for the charging process.

In the invention submitted herein, the active substance of the carbon minus electrode is carbon-graphite long-fiber material or a composition of carbon materials. All carbon material components of the minus electrode contain chemical or mechanical graphite compound with alkali metal, alkaline earth metal, magnesium or aluminum. The metal in the active substance of the minus electrode is tightly fixed and during the charge/discharge process it does not move. For the electrode process to take place, the required electric current is provided by the flow of anions in a non-water electrolyte. Thus equally even and good operation of the electrode is provided, irrespective of the applied metal at room temperature as well as in an increased and decreased temperature. As the proportion of the metal in the metal compound with graphite is in grammolecules, then, if metals, positioned close to each other in the periodical system of elements are applied, especially, if they participate in the electrochemical reaction of the process of charge/discharge by 2 or 3 electrons, from the energetical point of view these metals are practically equal and such metals as aluminum, magnesium, calcium,

sodium and even potassium do not significantly fall behind lithium, but are more easily available, less rare, cheaper.

Practically, the total amount of metal in the active substance of the electrode, determining the specific power capacity of the electrode, depends on the extent of graphitization of the active substance of the electrode and the properties of the electrolyte, which in turn depend on the constitution of the electrolyte composition, especially for desired additives.

Example 7

The active substance of the minus electrode of the high power capacity accumulator contains a chemical or mechanical compound of graphite with lithium. The proportion of the moles of carbon and metal in the active substance is determined by the formula Li_xC_6 , where $x = 1$.

The amount of the metal in the active substance of the minus electrode is from 4 to 9% of the weight.

Example 8.

The active substance of the minus electrode of the high power capacity accumulator contains a chemical or mechanical compound of graphite with sodium. The proportion of the moles of carbon and metal in the active matter is determined by the formula Na_xC_8 , where $x = 1$.

The amount of the metal in the active substance of the minus electrode is from 10 to 19% of the weight.

Example 9

The active substance of the minus electrode of the high power capacity accumulator contains a chemical or mechanical compound of graphite with potassium. The proportion of the moles of carbon and metal in the active substance is determined by the formula K_xC_8 , where $x = 1$.

The amount of the metal in the active substance of the minus electrode is from 12 to 28% of the weight.

Example 10

The active substance of the minus electrode of the high power capacity accumulator contains a chemical or mechanical compound of graphite with magnesium. The proportion of the moles of carbon and metal in the active substance is determined by the formula Mg_xC_9 , where $x = 1$.

The amount of the metal in the active substance of the minus electrode is from 8 to 17% of the weight.

Example 11

The active substance of the minus electrode of the high power capacity accumulator contains a chemical or mechanical compound of graphite with calcium. The proportion of the moles of carbon and metal in the active substance are determined by the formula Ca_xC_9 , where $x = 1$.

The amount of the metal in the active substance of the minus electrode is from 13 to 27% of the weight.

Example 12.

The active substance of the minus electrode of the high power capacity accumulator contains a chemical or mechanical compound of graphite with aluminum. The proportion of the moles of carbon and metal in the active substance are determined by the formula Al_xC_9 , where $x = 1$.

The amount of the metal in the active substance of the minus electrode is from 10 to 20% of the weight.

The prior art for the active substance of the plus electrode of the high power capacity accumulator is the patent WO JP 60-10465, where the active substance of the carbon plus electrode is a chemical compound of graphite with transitive metals, the degree of oxidation in the compound is +3 or lower. The structure of the active substance of carbon plus electrode is uniform. In the invention submitted herein all carbon components/materials contain a chemical or mechanical compound of graphite with a transitive metal, the degree of oxidation of the metal in the compound may be +3 and higher. It is most advantageous to apply such a transitive material as chromium,

manganese, iron or nickel in the compound. Metal in the active substance of the plus electrode is tightly fixed and does not move in the charge/discharge process.

Actually the total amount of metal in the active substance of the electrode determining the specific powercapacity of the electrode depends on the level of graphitization of the active substance of the carbon electrode and the properties of the electrolyte, which in turn depend on the contents of the electrolyte composition, especially the desired additives.

Example 13

The active substance of the carbon plus electrode of the high power capacity accumulator contains chemical of mechanical compound with iron. The proportion of carbon and metal grammolecules in the active substance are determined by the formula $\text{Fe}_x\text{C}_{16}\text{An}_y$, where $x = 1$, whereas $y = x \cdot Z_{\text{Me}}/Z_{\text{An}}$, where Z_{Me} - is the level of oxidation of the metal contained in the compound, Z_{An} - the size of anion charge. The amount of metal in the active substance of the carbon plus electrode, if the level of oxidation is conditioned as $Z_{\text{me}} = 0$, may be from 10 to 22% of the weight.

Example 14

The active substance of the carbon plus electrode of the high power capacity accumulator contains chemical of mechanical compound with chromium. The proportion of carbon and metal grammolecules in the active substance are determined by the formula $\text{Cr}_x\text{C}_{16}\text{An}_y$, where $x = 1$, whereas $y = x \cdot Z_{\text{Me}}/Z_{\text{An}}$, where Z_{Me} - is the level of oxidation of the metal contained in the compound, Z_{An} - the size of anion charge. The amount of metal in the active substance of the carbon plus electrode, if the level of oxidation is conditioned as $Z_{\text{me}} = 0$, may be from 8 to 21% of the weight.

Example 15

The active substance of the carbon plus electrode of the high power capacity accumulator contains chemical of mechanical compound with manganese. The proportion of carbon and metal grammolecules in the active substance are determined by the formula $\text{Mn}_x\text{C}_{16}\text{An}_y$, where $x = 1$, whereas $y = x \cdot Z_{\text{Me}}/Z_{\text{An}}$, where Z_{Me} - is the level of oxidation of the metal contained in the compound, Z_{An} - the size of anion charge. The

amount of metal in the active substance of the carbon plus electrode, if the level of oxidation is conditioned as $Z_{me} = 0$, may be from 8 to 21% of the weight.

Example 16

The active substance of the carbon plus electrode of the high power capacity accumulator contains chemical of mechanical compound with nickel. The proportion of carbon and metal grammolecules in the active substance are determined by the formula $Ni_xC_{16}An_y$, where $x = 1$, whereas $y = x \cdot Z_{Me}/Z_{An}$, where Z_{Me} - is the level of oxidation of the metal contained in the compound, Z_{An} - the size of anion charge. The amount of metal in the active substance of the carbon plus electrode, if the level of oxidation is conditioned as $Z_{me} = 0$, may be from 10 to 22% of the weight.

For the invention submitted herein of the high power capacity accumulator electrolyte the prototype has not been found. The electrolyte consists of three layers:

- electrolyte of the minus electrode space, with which the minus electrode has been impregnated/filled (2) and the separator of its side (3);
- electrolyte of plus electrode space, with which the plus electrode has been impregnated/filled (6) and the separator of its side (5);
- between both previously mentioned electrolytes of electrode space there is a film/membrane-electrolyte, which provides that the minus and plus electrode space electrolytes do not mix and do not loose their required properties.

The compositions of all three electrolyte layers are different. Depending on the requirements, with low voltage between the electrodes of the cell, the basic contents of the compositions can be diverse to a small extent, but the desired additives in the compositions of the separate layers will be different; with high voltage between the electrodes of the cell, the content of the compositions of different layers will significantly differ.

All three compositions of electrolyte layers have common properties:

- selective electroconductivity of anions, which is practically the same for all three layers; low mobility of the cations, practically all cations are tightly fixed;
- the electrolyte, the components of the composition of all three layers do not participate in the process of charging/discharging, but provide the electrical conductivity possibilities of the anions, necessary for the process to take place;

- the electrolyte stabilizes the operation of electrodes and helps to ensure their required, envisaged properties.

To provide the electrical conductivity of the electrolyte mainly anions F and Cl have been employed, but it is possible to apply also BF_4 and others. Compositions of electrolyte layers containing the following are more investigated:

- amines, polymers and substances containing them;
- substituted ammonium salts, polymers and substances containing them;
- metal salts and other desired additives.

Example 17

The electrolyte of high power capacity accumulator (Fig. 1, 2) consists of three layers:

- compositions of minus electrode space electrolyte layer (2, 3);
- compositions of plus electrode space electrolyte layer (5, 6);
- compositions of films/membranes-electrolytes (4).

Contents of the space electrolyte layer for the minus electrode:

- polyethylenpolyamine (the amino groups have been methylated in such a way that the tertiary amines of their total amount would make from 20 to 80%, the quaternary ammonium salt (chloride, fluoride) would make from 10 to 80%, tertiary ammonium salt (chloride, fluoride) would make from 0 to 20%) from 40 to 80%;
- triethylamine from 20 to 50%;
- trimethylamine from 0 to 40%;
- the desired additive, metal salt (chloride, fluoride) present in the active substance of the electrode from 0 to saturation.

Contents of films/membranes-electrolyte compositions:

- polyethylenpolyamine (from 10 to 80% the amino groups are crosslinked among themselves by methylene groups or in some other way and methylated in such a way that the tertiary amines

would make from 20 to 80% of the total amount of amino groups, quaternary ammonium salts (chloride, fluoride) would make from 20 to 80% the tertiary ammonium salts (chloride, fluoride) — from 0 to 20%)

- N,N¹-tetramethyldiamine from 5 to 45%;
- trimethylamine from 0 to 20%;
- desired additives, metal salts — AlCl₃ and/or others from 0 to saturation.

Contents of space electrolyte layer compositions for plus electrode:

- polyethylenpolyamine (amino groups are methylated in such a way that tertiary amine would make from 5 to 80% of the total amount of amino groups, quaternary ammonium salts (chloride, fluoride) would make from 5 to 90%, tertiary ammonium salts (chloride, fluoride) — would make from 0 to 20%) from 40 to 80%;
- triethylamine from 0 to 50%;
- trimethylamine from 0 to 40%;
- desired additives, metal salts (chloride, fluoride) present in the active substance of the electrode and/or others from 0 to saturation.

Applying the examples, described in the invention, submitted herein it is possible to create accumulators of practically any size and power capacity, different connections of their cell batteries, the specific power capacity of the latter being will be from 100 to 150 W.h/kg, but qualitatively and diligently developing the manufacturing technology and applying the most feasible variants it is possible to achieve the specific power capacity even up to 200-300 W.h/kg. The voltage of the accumulator battery, if a chain connection is applied, can be theoretically unlimited. The voltage between the electrodes of one cell may be from 1,5-2 V to 4-5 V.

It is possible to apply these accumulators of high power capacity with good results in transportation, electrical and electronic devices and domestic appliances.

Depending on the choice, the accumulators can be completely harmless to people and the environment.

AMENDED CLAIMS

[received by the International Bureau on 10 February 1998 (10.02.98);
original claims 1,3,5,6,16, and 20 amended;
remaining claims unchanged (6 pages)]

1. Accumulator, the elements thereof - positive and negative electrodes together with the electrolyte being enclosed into films or sheets, inert in relation to the electrodes and electrolyte welded together along the perimeter in the special welded area by the method of thermal compression; specific contact outlets being brought through the welded area, *characterized in that* the elements of the accumulator - positive and negative electrodes, made of long carbon fibre or composite from long carbon fibre and highly graphitized carbon, containing chemical or mechanical metal-graphite compound, and film/membrane electrolytes, covered from both sides by separators, made from the same or different materials, said electrodes, electrolytes and separators being worked into the frames along the perimeter, said frames of electrodes or parts thereof optionally made from electroconducting material, said frames of film/membrane electrolytes and separators made from electroinsulating material, together with electrolytes have been covered from both sides with thermoplastic or other suitable material films or sheets, inert in relation to the electrodes and electrolytes and, welding or gluing the frames together with a method feasible in any given situation, the covering films or sheets are welded or glued to the frames, the contact outlets of the electrodes, totally or partially made of the active components of the electrodes, being brought through the frames of the electrodes, into which the electrodes have been worked, in appropriate places.

2. Accumulator according to Claim 1, *characterized in that* its elements, which have been worked into the frames, together with the electrolytes are covered from both sides, as well as that the electrodes together with the electrolytes are separated with inert in relation to the electrodes and electrolytes thermoplastic or other suitable material films or sheets in required places and, welding or gluing the frames together, simultaneously the films or sheets are welded or glued to the frames.

3. Accumulator according to Claim 1, wherein between the contact outlets/collectors of the positive and negative electrodes a frame is formed, which serves to fix together and separate the positive and negative electrodes of the elements as well as its contact outlets/collectors, as well as to provide the outer packing of the accumulator, its sealing, *characterized in that* frames have been formed along the perimeter of the elements of the accumulator, positive and negative electrodes, film/membrane-electrolyte with separators, whereas the elements have been worked into the frame and the contact outlets/collectors have been brought through the frame in appropriate places, welding or gluing the frames, as well as the outer covering and if necessary, the inner, separating films or sheets together in the required order, said frames optionally modified by welding, forming or

surface covering, they ensure the fixing and necessary separation of the elements of the accumulator, as well as the exterior packing, its hermetic sealing.

4. The carbon negative electrode of the high power capacity accumulator with non-water electrolyte consisting of two layers - the interior, which contains iron group metals to increase the electric conductivity and thus the density and stability of charge/discharge current, and the exterior one, which does not contain iron group metals and performs the function of the active substance of the negative electrode in charge/discharge processes, *characterized in that* the carbon negative and positive electrodes of the high power capacity accumulator with non-water electrolyte contain throughout a chemical or mechanical compound of iron group metal or other metal with graphite to increase its electroconductivity and thus increasing the density of charge/discharge current and achieving the operation stability of the accumulator, whereas the chemical or mechanical compound of metal with graphite performs the functions of the active substance of the electrode in charge/discharge processes.

5. The carbon electrodes of the high power capacity accumulator with non-water electrolyte according to Claim 4, *characterized in that* the positive and negative electrodes are made of long carbon fibres or composite from long carbon fibres and highly graphitized carbon, which contain throughout a chemical or mechanical compound of iron group metal or other metal with graphite to increase its electroconductivity, while this compound performs the functions of the active substance of the electrode, are manufactured from carbon-graphite long-fiber cardboard, felt or woven material and perform the functions of contact outlets/collectors of the electrodes.

6. The active substance of carbon negative electrode of the high power capacity accumulator with non-water electrolyte is a chemical compound of graphite and alkali, whereas the material of the electrode consists of two different components/phases- high graphite content carbon and short-fiber material, - carbon soot, both components/phases have been used to obtain the compound of graphite with metal, *characterized in that* the negative and positive electrodes of the high power capacity accumulator with non-water electrolyte, which contain the active substance graphite and metals chemical or mechanical compound, said metals being firmly fixed in the electrodes material to prevent the movement of metals and ions thereof from the electrodes into electrolytes or vice versa at charging/discharging, the charging/discharging process in electrodes secured by selective anion movement, consist of two different components/phases - high graphite content carbon and long-fiber carbon-graphite felt, cardboard or woven material, which have been applied to obtain a compound of graphite with metal.

7. The active substance of carbon negative electrode of the high power capacity accumulator with non-water electrolyte according to Claim 6, *characterized in that* in the active substance of the negative carbon electrode, graphite and metal chemical or mechanical compound an alkaline metal - sodium is present.

8. The active substance of carbon negative electrode of the high power capacity accumulator with non-water electrolyte according to Claim 6, *characterized in that* in the active substance of the negative carbon electrode, graphite and metal chemical or mechanical compound an alkaline metal - potassium is present.

9. The active substance of carbon negative electrode of the high power capacity accumulator with non-water electrolyte according to Claim 6, *characterized in that* in the active substance of the negative carbon electrode, graphite and metal chemical or mechanical compound an alkaline-earth metal is present.

10. The active substance of carbon negative electrode of the high power capacity accumulator with non-water electrolyte according to Claim 9, *characterized in that* the graphite and metal compound the alkaline-earth metal is calcium.

11. The active substance of carbon negative electrode of the high power capacity accumulator with non-water electrolyte according to Claim 6, *characterized in that* in the graphite and metal chemical or mechanical compound magnesium is contained.

12. The active substance of carbon negative electrode of the high power capacity accumulator with non-water electrolyte according to Claim 6, *characterized in that* in the graphite and metal chemical or mechanical compound aluminum is contained.

13. The carbon negative electrode of the high power capacity accumulator with non-water electrolyte according to any of Claims 6 - 12, *characterized in that* the carbon negative electrode, the active substance of which is a graphite and metal compound consists only of long-fiber carbon-graphite material, which is used to obtain metal chemical or mechanical compound of the active substance with graphite.

14. The carbon positive electrode of the high power capacity accumulator with non-water electrolyte consists of carbon graphite long-fiber paper, cardboard, felt type material, *characterized in that* the positive and negative carbon electrodes are of carbon-graphite long-fiber paper, cardboard, felt type material, which is applied to obtain a chemical or mechanical graphite and metal compound of the active substance.

15. The carbon positive and negative electrodes of the high power capacity accumulator with non-water electrolyte according to Claim 14, *characterized in that* the

carbon-graphite long-fiber material, applied to obtain a chemical or mechanical graphite and metal compound of the active substance is woven.

16. The carbon positive electrode of the high power capacity accumulator with non-water electrolyte contains the active substance - a chemical or mechanical compound of graphite and transitive metal, where the metal is in lower oxidation levels, the level of oxidation is +3 and lower, *characterized in that* the positive carbon electrode contains active substance - a chemical or mechanical compound of graphite with a transitive metal, where the metal is in higher levels of oxidation, the level of oxidation is +3 and higher, said metal being firmly fixed in the electrode material to prevent the movement of metals and ions thereof from the electrodes into electrolytes or vice versa at charging/discharging, the charging/discharging process in electrodes secured by selective anion movement.

17. The carbon positive electrode of the high power capacity accumulator with non-water electrolyte according to Claim 16, *characterized in that* the transitive metal of the chemical or mechanical compound of the transitive metal and graphite, contained in the active substance of the carbon positive electrode is chromium and its level of oxidation is +3 and higher.

18. The carbon positive electrode of the high power capacity accumulator with non-water electrolyte according to Claim 16, *characterized in that* the transitive metal of the chemical or mechanical compound of the transitive metal and graphite, contained in the active substance of the carbon positive electrode is manganese and its level of oxidation is +3 and higher.

19. The carbon positive electrode of the high power capacity accumulator with non-water electrolyte according to Claim 16, *characterized in that* the transitive metal of the chemical or mechanical compound of the transitive metal and graphite, contained in the active substance of the carbon positive electrode is iron and its level of oxidation is +3 and higher.

20. The carbon positive electrode of the high power capacity accumulator with non-water electrolyte, the active substance of which is a chemical compound of graphite with nickel and it is in the form of carbon-graphite long-fiber material, *characterized in that* for the carbon positive electrode long-fiber carbon-graphite material, containing the active substance - chemical or mechanical compound of graphite with chrome, is used, said metal being firmly fixed in the electrode material to prevent the movement of metals and

ions thereof from the electrodes into electrolytes or vice versa at charging/discharging, the charging/discharging process in electrodes secured by selective anion movement.

21. The carbon positive electrode of the high power capacity accumulator with non-water electrolyte according to Claim 20, *characterized in that* the graphite long-fiber material, containing active substance - graphite and manganese chemical or mechanical compound is applied in it.

22. The carbon positive electrode of the high power capacity accumulator with non-water electrolyte according to Claim 20, *characterized in that* the graphite long-fiber material, containing active substance - graphite and iron chemical or mechanical compound is applied in it.

23. The high power capacity accumulator with non-water electrolyte, where a separator for parting the electrodes from inert material in relation to the electrodes and electrolyte has been placed between the positive and negative electrodes, *characterized in that* between the positive and negative electrodes two thin separators from inert material in relation to the electrodes and electrolyte have been placed and between them a film/membrane-electrolyte is situated, which together with separators separate the electrodes and their space electrolytes, whereas the separators separate the electrodes from film/membrane-electrolyte.

24. The high power capacity accumulator with non-water electrolyte, where two thin separators have been placed between the positive and negative electrodes, is characterized according to Claim 23, *characterized in that* between the separators, parting the electrodes, there is a film/membrane-electrolyte, whereas the separators on each side of the films/membranes-electrolytes, according to the need, may be of the material of different composition or/and structure.

25. The non-water electrolyte of the high power capacity accumulator comprising three electrolyte layers of different composition:

- composition of the space of the positive electrode;
- composition of the space of the negative electrode;
- composition of the film/membrane-electrolyte,

wherein all three electrolyte compositions have close selective anion electroconductivity, whereas the film/membrane-electrolyte separates the electrolyte of the positive electrode from the electrolyte of the negative electrode, not allowing them to mix and alter the required properties, the components of the electrolyte compositions do

not participate in the processes of charging/discharging of the accumulator, the anion does not oxidate or reduce either, but ensures the envisaged electroconductivity, the required properties of electrolyte compositions and helps to provide the properties of the electrodes.

26. The high power capacity accumulator with non-water electrolyte according to Claim 25, *characterized in that* in the compositions of all three different electrolytes include the following:

- amines, polymers, containing them;
- substituted ammonium salts, polymers and substances, containing them;
- metal salts and other desired additives,

the contents of the compositions has been selected in such a way as to maximally fix the metal, contained in the active substance of the electrode, graphite and metal chemical or mechanic combination, in the active substance itself; to fix the cations, contained in the electrolyte and complex anions, formed by them, to maximally increase and ensure uniformity of the selective conductivity of the anions, present in all three electrolyte compositions and ensure the required mechanical properties of the electrolyte compositions.

Fig. 1

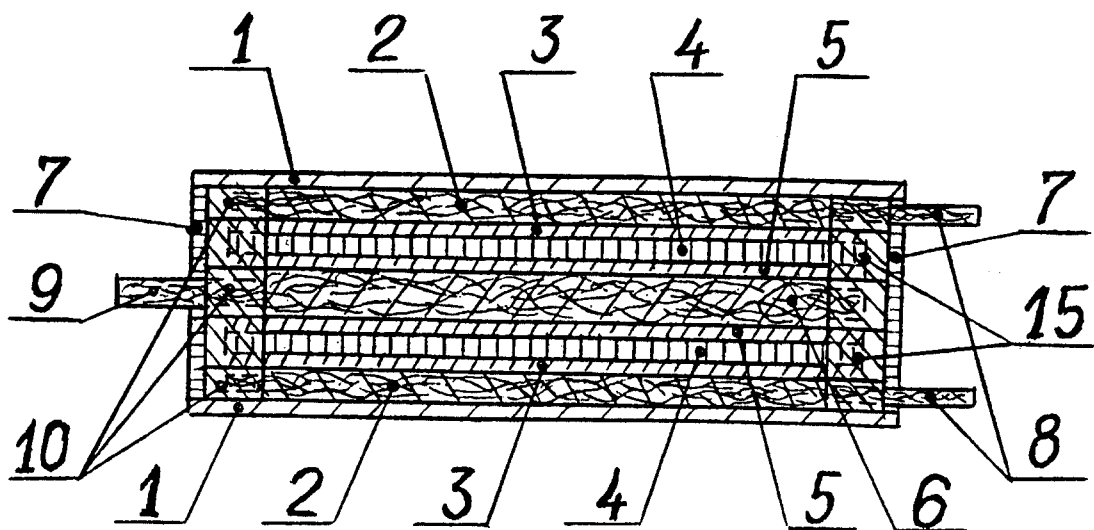


Fig. 2

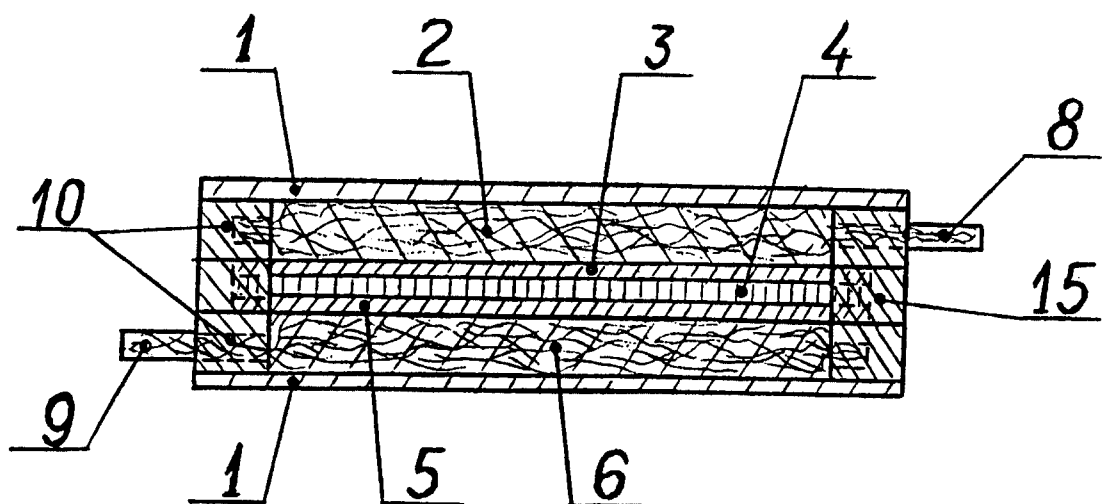


Fig.3

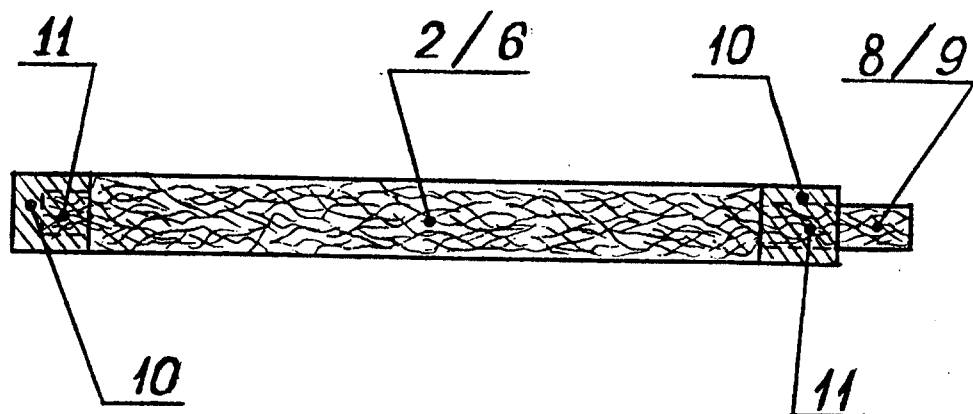


Fig.4

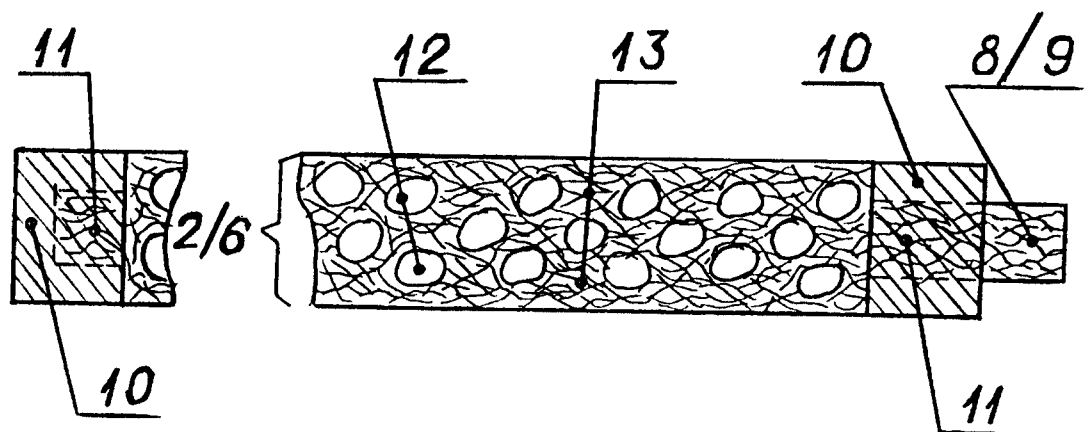


Fig.5

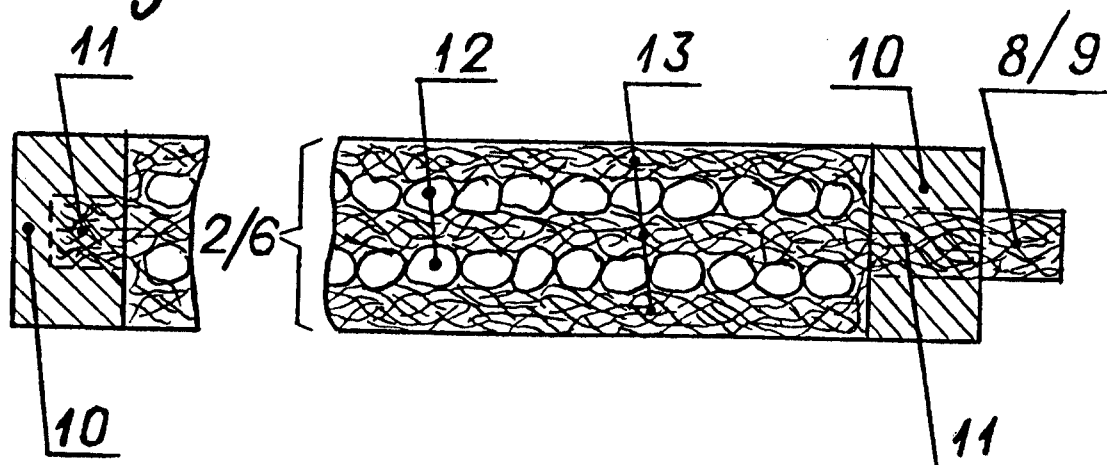


Fig. 6

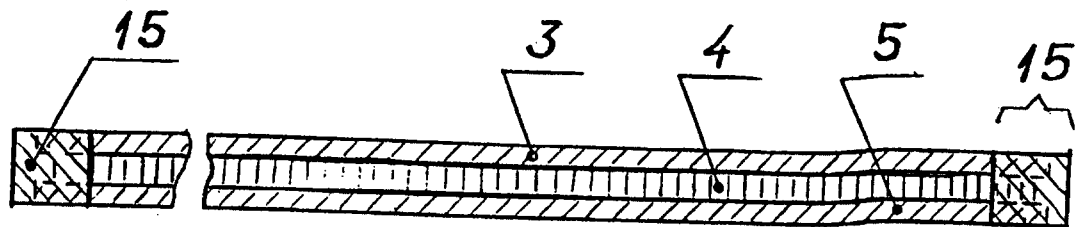


Fig. 7

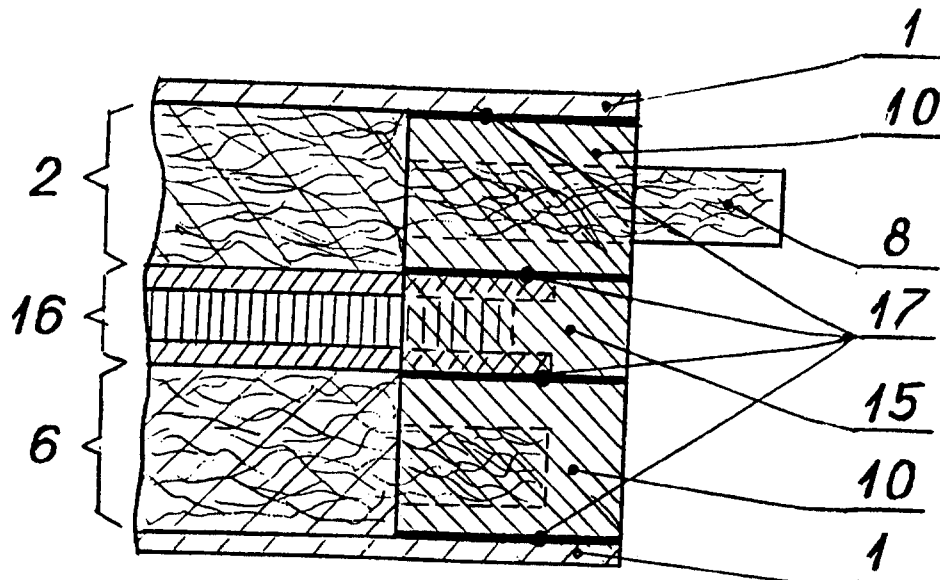


Fig. 8

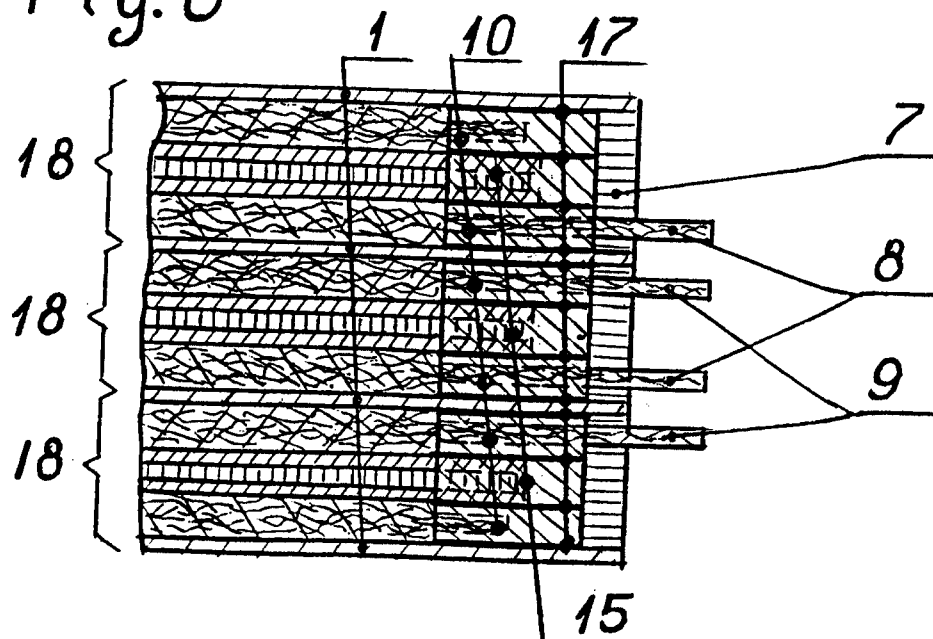
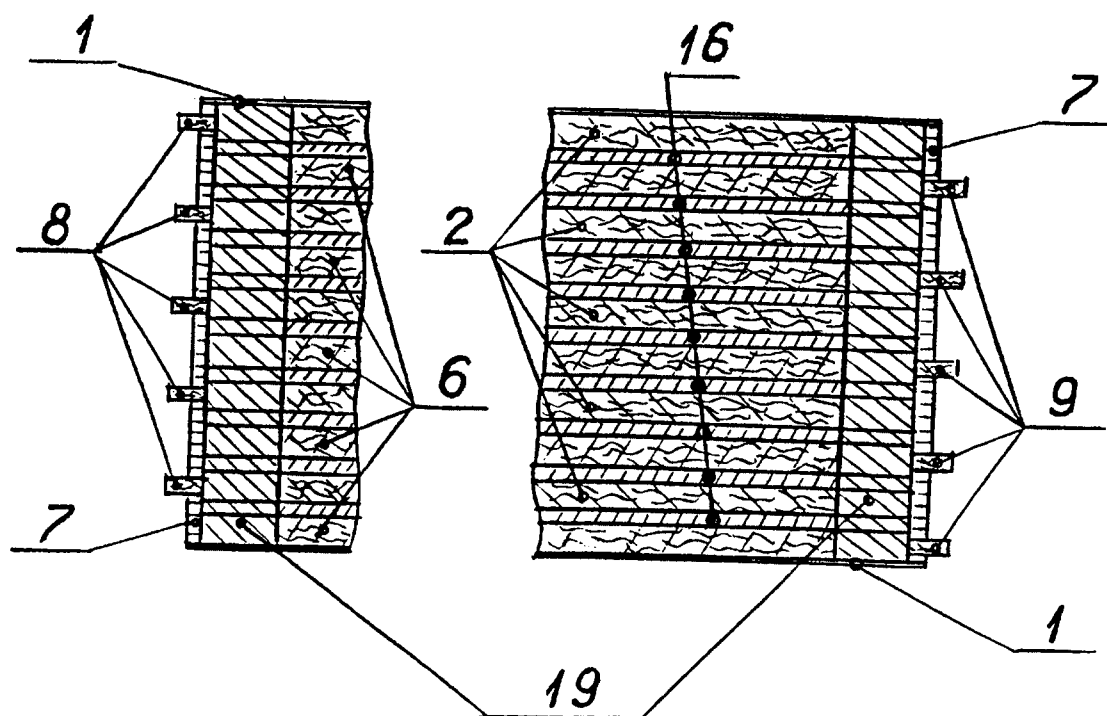


Fig. 9*Fig. 10*