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(54) Process for preventing fouling and corrosion of a structure..

(57) Process for preventing fouling an corrosion of a structure which comprises covering the water-contacting surface of an underwater structure equipped with electrical corrosion inhibiting means or electrochemical corrosion inhibiting means with a plurality of anti-fouling metal tiles in such a manner that said metal tiles contact said water-contacting surface via an electrical insulated layer in the direction perpendicular to said water-contacting surface but do not contact one another in the direction of the water-contacting surface.

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Background of the Invention:

The present invention relates to a process for preventing adhesion of marine organisms to a metal structure such as ship, dolphin, gate and underwater structure (hereinafter referred to as prevention of fouling) and preventing corrosion of said metal structure.

Additionally, since it is a structure coming into constant contact with seawater, the following description will be made by way of example, with reference to the case where the structure is used in seawater.

Heretofore, a method of preventing fouling of a structure has been exclusively depending on the use of anti-fouling paint. This anti-fouling paint includes, for example, metals such as cuprous oxide and organic tin, by gradual elution of which, the object of preventing fouling has been attained.

These anti-fouling paints have been, however, not free from drawbacks in that an underwater structure (structure used in water) have been required to be docked at every 1 - 2 years for repainting. Especially, in the case of a ship, metals such as cuprous oxide elutes together with rosin for curbing the eluted amount and a skeleton remaining after elution becomes increasingly obstructing elution, that results in gradual reduction of the anti-fouling effect and in addition, due to this skeleton, the surface roughness of the hull increases, causing increase of the hull resistance.

Due to that, it has been conceived to cover the hull with an anti-fouling and anti-corrosion metal material. At present, small ships whose hulls are made of Cu-Ni for preventing fouling are being built in Europe, which has been introduced in literatures and the like. However, in this case, when steel and Cu-Ni are electrically connected in seawater, the steel is corroded severely due to electric corrosion. This leads to countermeasures such as covering the entire submerged (submarine) part of the structure with Cu-Ni or completely electrically insulating Cu-Ni from the steel segment. Not only in the case of a ship, but in the case of a structure used in seawater, depending on whether the metal covering the surface of such structure is base or noble as compared with the anti-fouling metal material, it is decided whether the ship or the structure used in seawater is exposed to the danger of corrosion or corrosion of the anti-fouling metal material is expedited. Generally, however, a metal which is base as compared with the anti-fouling metal material is used in the structural material of a ship and other structures and complete insulation between the two or complete covering of the surface of the ship or other structures with the anti-fouling metal material is the indispensable requirement. However, in such case, if there is an inconvenience and the anti-fouling metal and the structure are electrically short-circuited, corrosion is abnormally expedited.

Due to this, it is conceivable to cover the surface of a structure (hereinafter a ship and a structure used in seawater shall be referred to by this name en masse) with a metal that is base as compared with the anti-fouling metal such as, for example, zinc and aluminium alloys or equip the structure with a device capable of supplying an electric current from outside.

However, in such case, the following inconvenience is caused.

Namely, as shown in Fig. 1 of the accompanying drawings, where a structure 1 covered with an anti-fouling metal 3 via an insulated layer 2 contacts seawater 4 at the surface of the anti-fouling metal 3, there is a portion 5 that cannot be covered where the insulated layer is defective, such as, for example, an uneven portion of the welded segment, and when from one reason or another, for example, due to an outer force, the anti-fouling metal 3 contacts the structure 1 to produce a short-circuited portion 6, from the above-referred defective portion 5, a galvanic current i_g flows to the anti-fouling metal, expediting corrosion of the structure 1 at a rapid speed.

To prevent this, it is necessary to reduce the potential of the anti-fouling metal to that of the structure 1 to thereby eliminate the potential difference. For that end, by equipping an anode consisting of a base metal, for example, a zinc anode 7 electrically contacting the structure 1, thereby causing a current i_p to flow from the zinc anode 7 to the anti-fouling metal 3, it is possible to prevent it in principle.

However, in such case, the anti-fouling metal 3 is negatively polarized, that stops supply of anti-fouling ion necessary for preventing fouling (the anti-fouling metal corrodes while slightly releasing metal ions, allowing marine organisms to start adhering. In addition, as shown in Fig. 1, when the surface of the structure is covered with a large sheet of an anti-fouling metal (meaning it is electrically connected to the surface), even if one place is short-circuited no matter what location between the structure 1 and the anti-fouling metal 3 it may be, the entire surface of the anti-fouling metal runs into such inconvenience, moreover, flowing a current to the entire surface of the anti-fouling metal, and so, there is an inconvenience that a huge quantity of zinc has to be equipped.

On the other hand, however, when a structure consisting of such naked metal is in seawater, what is different from a painted metal structure such as the conventional ship and underwater structure, is a very low electrical resistance (or electrochemical resistance) of the surface that contacts seawater. This has a very important significance at present when use of electrical energy has developed remarkably. Namely, almost all steel structures where a ship comes alongside such as quay (wharf), dolphin and another ship has been electrically made corrosion-resisting, in the vicinity of which an electric field (or fields) due to flow of a current (called a stray current) has been formed. In addition, another electric field is formed due to a current leaked from a railway track.

When there is a naked metal within such electric fields, a current flows in a portion at a high potential and flow out from a portion at a low potential. The portion from which the current flows corrodes. On the other hand, the portion to which the current flows in is negatively polarized and corrosion of the metal is curbed, but the metal loses the effect of curbing (adhesion of) organisms.

The pattern of this situation is shown in Fig. 2, which illustrates a case wherein there is a metal plate 8 (length Lm) parallel to the direction of a potential gradient in seawater at a degree of potential gradient of V volt/Lm, wherein a current of 1 A flows. In such case, the current flows in portion A of the metal 3 and flows out from portion B.

At this time, at portion A and portion B, generally the following reactions take place.

Portion A:

$$\frac{1}{2} O_2 + H_2O + 2e \rightarrow 2OH \qquad (1)$$

Portion B:

$$M \rightarrow M^{n+} + ne^- \qquad (2)$$

Explaining now with regard to the case of using copper as a metal plate, the effect of this metal of preventing adhesion of marine organisms (to the surface thereof) is due to copper ion produced upon corrosion of copper, formation of metallic copper ion due to the equation (2) is preferable from the viewpoint of anti-fouling effect, however, the reaction occurring at the portion A has nothing to do with formation of copper ion, formation of OH^- (hydroxyl group ion) curbs corrosion of copper, which is a phenomenon that is not preferable from the viewpoint of curbing adhesion of (marine) organisms.

In general, in a metal plate in seawater, it is preferable that the reaction points of the equations (1) and (2) occur uniformly and this occurring points alternate momentarily, and when this condition is met, the metal plate would be uniformly corroded, which metal plate may be said to be a very preferable metal material from the viewpoint of preventing fouling. One more requirement necessary for the metal material to meet is that it should have a corrosion velocity to an extent of generating metal ion effective for preventing fouling. Excessive elution is not preferable from the viewpoint of the durability.

Even if a metal plate or material which meets such requirements and is very effective for preventing fouling, is obtained, it may be said to be a fate of a ship that is is used under the aforementioned environment of the surface of the sea subjected to the electric fields.

When an excellent conductive metal material is used for a large and long object such as ship, reasons for obstructing uniform dissolution of a metal include the following, aside from the aforesaid external reasons.

(a) Generation of macrocell current

Between remote positions contacting the respective parts of the hull where there are large differences such as ununiformity of concentrations of dissolved oxygen, a temperature difference and a difference in a flow rate in seawater, the reactions of the above-referred equations (1), (2) would occur.

(b) The ship propeller consists of a copper alloy, and in order to prevent galvanic corrosion coacting with the hull (consisting of steel), it is necessary to practice electrical prevention of corrosion by a current-flowing anode (zinc) or an external power source system, but this would generate distribution of potentials on the hull.

(c) When a ship anchors, as shown in Fig. 3, upon lowering an anchor, a current would be generated from anti-corrosion zinc provided at the stern.

In Fig. 3, reference numeral 9 shows a steel hull, numeral 7 anti-corrosion zinc, numeral 11 a copper alloy propeller and numeral 12 a steel anchor. As will be seen in Fig. 3, a potential difference of about 400 mv between the anti-corrosion zinc 7 and the anchor 12 causes a current to flow in the direction of arrows.

A large-size ship such as a crude oil tanker, a bulk carrier or the like has a ship length extending as long as 200 - 300 m, so a slight potential gradient of 1 mv/m will bring about a potential difference of 0.1 v over a length of 100 m, and in such a case a flow-in and flow-out current of $10\mu A/cm^2$ has been observed by actual measurement.

By this, the corrosion velocity of copper at a part from where the current flows out (portion B of Fig. 2) is calculated as follows: Assuming that the current of $1\ \mu A/cm^2$ flows in a day, it will wear the plate thickness by 6.1×10^{-5} mm. This amounts in a year to $6.1 \times 10^{-5}/(\mu A/cm^2)$ D x $10\ \mu A/cm^2$ x 365 days. That is, the corrosion velocity is equal to 0.22 mm/year. Assuming now that natural corrosion velocity in the absence of a flow of the current is 0.005 mm/year, then we obtain:

$$\frac{0.22 \text{ mm/year}}{0.005 \text{ mm/year}} \fallingdotseq 40$$

This means acceleration of about 40 times.

As mentioned above, existence of even such a slight potential gradient gives a very large influence over a large ship whose hull is covered with a naked metal plate or plates.

Brief Description of the Drawings:

Fig. 1 is a cross-section view of a model of an outer plate, showing the mode of a short-circuit accident and prevention of corrosion of a structure used in seawater. Fig. 2 is a cross-section view of a model of an outer plate, showing the route of a stray current in a metal plate within seawater having a potential gradient. Fig. 3 is a side elevation view of a ship showing one example of the route of a current (stray current) generated in the hull of the ship. Fig. 4 is a schematic side elevation view of a ship according to a first embodiment of the present invention. Fig. 5 is a fragmentary view of Fig. 4 taken along line V - V as viewed in the direction of arrows. Fig. 6 is a schematic side elevation view of a ship according to a second embodiment of the present invention (wherein a part of the anti-fouling metal plate is omitted). Fig. 7 is a cross-section view of a model of an outer plate for explaining corrosion caused by a short-circuit between a broad anti-fouling metal plate and a structural (construction) material as well as prevention of such corrosion. Fig. 8 is a cross-section view of a model of an outer plate for explaining the state at the time of a short-circuit according to a third embodiment of the present invention. Fig. 9 is a cross-section view of a model of an outer plate for explaining the effect of the present invention.

1 . . Structure, 2 . . Insulated layer, 3 . . Anti-fouling metal, 4 . . Water (seawater or fresh water), 6 . . Short-circuited portion, 7 . . Zinc anode

Detailed Description of the Invention:

An object of the present invention is to provide a process for preventing fouling and corrosion of a structure that has eliminated the aforesaid drawbacks of the conventional processes. The gist of the present invention resides in a process for preventing fouling and corrosion of a structure which comprises covering the water-contacting surface of an underwater structure equipped with an electrical corrosion inhibiting means or electrochemical corrosion inhibiting means with a plurality of anti-fouling metal tiles in such a manner that said metal tiles contact said water-contacting surface via an electrical insulated layer in the vertical direction of said water-contacting surface but do not contact one another in the direction of the water-contacting surface.

It is to be noted that the above-referred electrical corrosion inhibiting means involves a method of preventing corrosion of a structure by applying a DC voltage between a part intended to make anti-corrosive (structure) and serving as a cathode and a graphite or cast iron piece serving as a dummy anode, or by applying a DC voltage to a platinum-plated titanium electrode or an insoluble anode such as Pb/Ag alloy anode to make the structure anti-corrosive, and the means also includes an automatic potential control device for automatically maintaining the potential of the structure.

In addition, the above-referred electrochemical corrosion inhibiting means involves a method of contacting with the structure, a metal exhibiting a potential baser than that of the material of the structure (for example, for a steel structure, Zn, Al, Mn and their alloys and pure Fe) to form an electric circuit of structure/water/base metal, and as a result the base metal melts instead of the structure, whereby corrosion of the structure is prevented.

The above-referred underwater structure means all structures contacting seawater or fresh water including ships and marine structures. The above-referred water-contacting surface means the surface of the structural member contacting (or adapted to contact) seawater or fresh water.

Hereinbelow, the present invention will be explained through analysis of the points of problems.

The density of a current generated by a potential gradient may be approximated by the following equation according to the results of my study.

$$i = \frac{E}{r_c} \cdot L \qquad (3)$$

where: i is a current density (A/cm^2)

E is a potential gradient per unit length (V/100 cm)

L is a length of a metal plate

r_c is an electrochemical reaction resistance (Ω-cm) of the equation (1) $(\frac{\eta}{i})i$

where: η is an overvoltage (V) of an anti-fouling metal

i is a current density (A/cm^2)

As would be apparent from the equation (3), in order to decrease a harmful current, it is effective to increase r_c or decrease L, but, since r_c is dependent upon physical properties of a metal, the practical method of settling is to decrease L.

Specifically, it is to use an anti-fouling metal on the outer surface of a hull, not in a huge form, but in many small cut forms.

The corrosion current density i_n of a metal plate is given as follows when it has a length L and being cut to n small plates.

$$i_n = \frac{E}{r_c} \cdot \frac{L}{n} \qquad (4)$$

From the equations (3), (4), a decreasing ratio f of the current density is given as follows.

$$f = \frac{i_n}{i} = \frac{1}{n} \qquad (5)$$

Thus, it is possible to reduce the current density to 1/n.

What value should be selected as the value of this n is an important problem. When the value of n is made too large, it would excessively shorten the length of one side of an anti-fouling metal, bringing about disadvantages such as complicated execution and increased cost of construction due to increase of cut portions (sealing of joints would be required therefor) and increased frictional resistance due to increase of joints. Generally, it is practically preferable to select the value of n such that i_n may have the upper limit of the permissible current density at about the same corrosion velocity as the natural corrosion velocity by taking into account the influence over the life of the anti-fouling metal and the fouling preventing effect. (The corrosion velocity doubles.)

When the entire length of a ship is L, the length of one cut out piece of anti-fouling metal is ℓ, the ratio of the permissible current density (density of corrosion current (i_n)/ natural corrosion current density (i_o) is k and the potential difference over the entire hull length is V_L volt, the following equation (6) is fulfilled.

$$\ell = k \cdot i_o \cdot L \cdot r_c / V_L \qquad (6)$$

For example, when k = 1, $r_c \approx 10^4 \Omega$--cm, V_L = 0.4 volt and $i_o \approx 0.25 \times 10^{-4}$ A/cm^2, the length ℓ of one cut out piece of anti-fouling metal and the influence of the hull length thereover become as follows.

Hull length (L cm)	Length of an anti-fouling metal piece (ℓ cm)
200×10^2	125
100×10^2	62.5
50×10^2	81.5
10×10^2	6.25

The numerical values shown above are presented for explaining the trend when there is a potential difference of 0.4 V between the both ends of a hull length from the bow to the stern. Actually, however, depending on the fitting position and number of anti-fouling zinc pieces, the hull length and the propeller as shown in Fig. 3, the potential gradient varies. And it is necessary to decide the length ℓ after taking into account these factors.

The aforesaid explanation is limited to the setup in the lengthwise direction of the ship only, however, the same theory is applicable to a setup in the widthwise direction (cross-sectional direction) of the ship as well. However, if it is taken into account that the length in the widthwise direction of the ship is only a fraction of the length from the bow to the stern, and also if the period during which it is influenced by a potential gradient is taken into account, then the cause due to the ship per se as mentioned in (b) above, sustains extremely longer than the external cause such as quay (wharf), pontoon and mooring. Namely, as compared with the mooring period which is normally several days, what is due to the ship per se always exists irrespective of sailing or anchoring, and further, the degree of influence in the widthwise direction is almost zero compared with that in the lengthwise direction from the structure of a ship. From these reasons, there is no strict restriction with respect to the length ℓ as compared to that in the widthwise direction.

Taking these points into account, embodiments of an anti-fouling ship covered with anti-fouling metal plates (tiles) are shown in Fig. 4, Fig. 5 and Fig. 6.

Fig. 4 shows an embodiment wherein anti-fouling metal tiles 14A each having a thickness of 0.2 - 0.3 mm and a length of ℓ cm are fitted in the lengthwise direction of a hull 9 via a gap space 15, which is cut in the widthwise direction at a portion 16 shown in Fig. 5. It is necessary to make the interval at the joint 15 of the anti-fouling metal tiles 14 and at the gap 16 as narrow as possible (less than several mm) and seal it with a water-proof insulating material. The anti-fouling metal plate 14A is adhered to the hull 9 with, for example, an adhesive via a proper insulated layer 18.

Fig. 6 shows an embodiment wherein metal plates cut into small pieces also along a lengthwise direction of the ship, are fitted on the surface of the hull. It is possible to properly select the processes shown in these embodiments according to the size of a ship.

Now, when the hull and the anti-fouling metal plate are short-circuited from some reason or another, a galvanic current flows between the hull and the anti-fouling metal, and the hull is corroded as mentioned previously. Here, a further detailed explanation will be given. In such case, by providing anti-corrosion zinc plate 7 shown in Fig. 1, the current i_p flows into the anti-fouling metal plate so as to reduce the potential of the anti-fouling metal plate to that of the hull to prevent corrosion. However, when the anti-fouling metal plate is not divided to fine plates or tiles, a huge current is required and practically it is almost impossible to prevent corrosion. This is a very important problem from the viewpoint of the safety of the ship, and by cutting the anti-fouling metal plate into many fine plates or tiles, it suffices to supply the current to an electrically short-circuited metal plate only. Since this can be done with a small quantity of the current, the aim is easily attainable. When the anti-fouling metal plate is not cut into many fine plates or tiles, a serious result would occur regardless of at what one location the anti-fouling metal may contact the hull. However, when the anti-fouling metal plate is cut to many small plates or tiles, it is possible to eliminate such danger. That is, many small plates of the same shape around the short-circuited anti-fouling metal plate function as conductors better than seawater and serve to reduce the potential quickly.

The mode of operation will be explained in more detail with reference to Fig. 7 and Fig. 8.

Fig. 7 is a simplified illustration where the anti-fouling metal plate that is not cut to many small plates or tiles is short-circuited to the hull, in which reference numeral 9 denotes a hull, numeral 13 denotes an electrical insulated layer, numeral 14 denotes an anti-fouling metal, numeral 7 denotes a metal that is baser than the metal of the hull with respect to a potential such as, for example, zinc, aluminium or the like, numeral 17 denotes a short-circuited portion of the anti-fouling metal 14 and the hull 9, and numeral 18 denotes a defective portion of painting or the like of the hull. In such case, from the metal that is baser than the steel constituting the hull, for example, Zn 7, a current i_p flows into the anti-fouling metal 14 to work so as to curb generation of i_g (a corrosion current flowing from the defective painted portion of the hull 18 to the anti-fouling metal 14). However, a huge quantity of the current is required therefor and depending on the relative positions of the short-circuited portion 7 and the defective painted portion 18 of the hull, it is not possible to stop i_g.

Fig. 8 shows a case of replacing the anti-fouling metal plate 14 of Fig. 7 by many divided small plates 14A, where a current i_p corresponding to the area of the short-circuited portion 17 only of the anti-fouling metal 14B is sufficient. The current passes succeedingly through the anti-fouling metal plates 14A which have low electrical resistances from seawater which has a high electrical resistance, thus quickly reduces the potential of the anti-fouling metal 14B and eliminates the current i_g generated from the defective portion 18.

As mentioned above, the process according to the present invention involves covering the water-contacting surface of a metal ship or a structure contacting water with many small anti-fouling metal plates or tiles which are cut out from a large anti-fouling metal plate via an electrical insulated layer, so that by keeping a ship or a structure used in sea-water in constant contact with a metal that is baser than the metal constituting the water-contacting surface of the ship or the structure, the process makes it possible to prevent abnormal corrosion of the anti-fouling metal material and incomplete foul preventing effect when there is a potential gradient, and at the same time, to prevent occurrence of abnormal corrosion of the hull due to accidental contact between the anti-fouling metal material and the structure or the ship hull.

Instead of a metal exhibiting a base potential, an insoluble anode such as platinum-plated titanium electrode or a lead-silver alloy electrode and a DC power source may be used, and even when an automatic potential control device for automatically keeping the potential of the structure is used, its functional effect is the same in principle.

To practice more efficiently the present invention, it is preferable to fit the aforesaid base metal in such a manner as to surround a ship or structure used in seawater. This is because by so doing, as shown in Fig. 9, a by-pass effect for a stray current i_g that is flowing when the structure is exposed to the electric field on the surface of the sea, is brought about, and at the same time, an effect of making even the distribution of potentials on the structure is brought about.

The foregoing effect is not limited to a huge outfit like a ship only, but it is also similarly effective to a huge watergate or a coastal structure which is large in the direction of the depth too.

It goes without saying that means of covering an anti-fouling metal is not restricted to adhesion of plates or tiles only, but said metal plates or tiles may be flame sprayed or plated as well.

WHAT IS CLAIMED IS:

1. A process for covering a structure with anti-fouling metal plates which comprises covering the water-contacting surface of an underwater structure equipped with electrical fouling inhibiting means or electrochemical fouling inhibiting means with a plurality of anti-fouling metal tiles in such a manner that said metal tiles contact said water-contacting surface via an electrical insulated layer in the direction perpendicular to said water-contacting surface but do not contact one another in the direction of the water-contacting surface.

2. An underwater structure, which comprises at least one of electrical fouling inhibiting means and electrochemical fouling inhibiting means equipped on said structure which contacts water, an electrically insulated layer provided on the surface of the outer plate of a submerged portion of said structure to shut off the conduction between said outer plate and water, and a plurality of anti-fouling metal tiles provided on said electrically insulated layer so as not to contact one another.

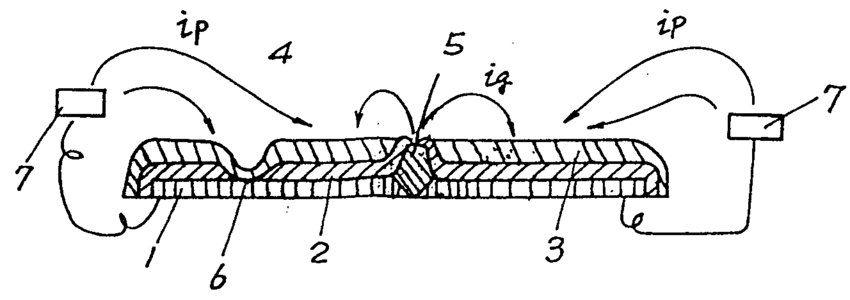

Fig. 1

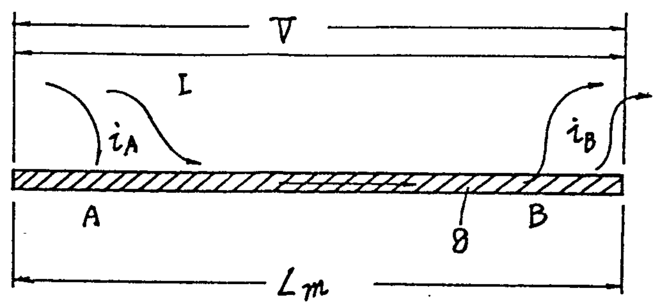

Fig. 2

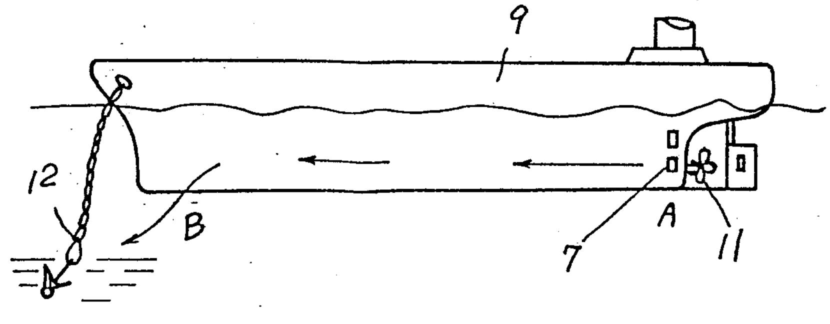

Fig. 3

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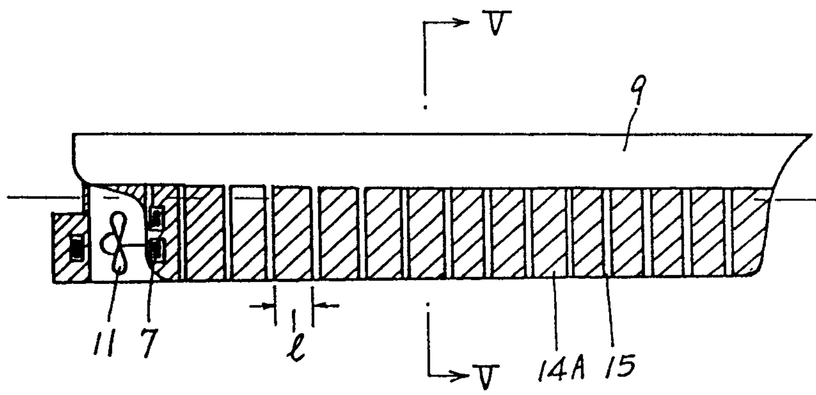

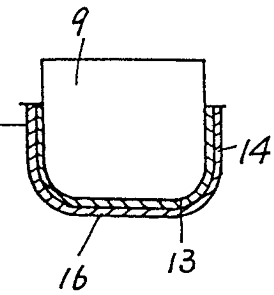

Fig. 5

Fig. 4

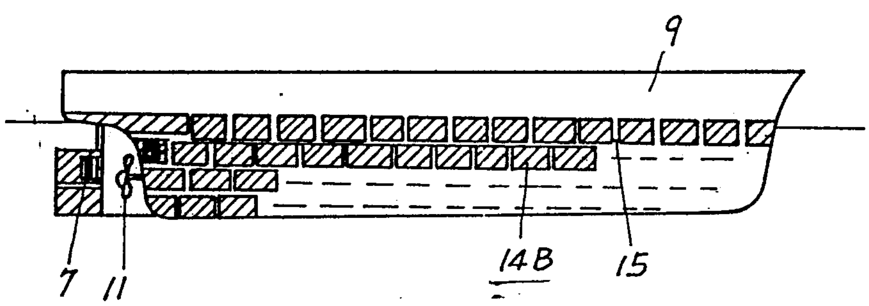

Fig. 6

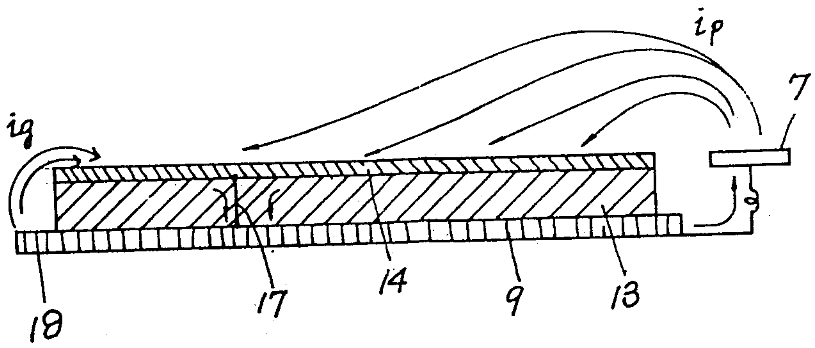

Fig. 7

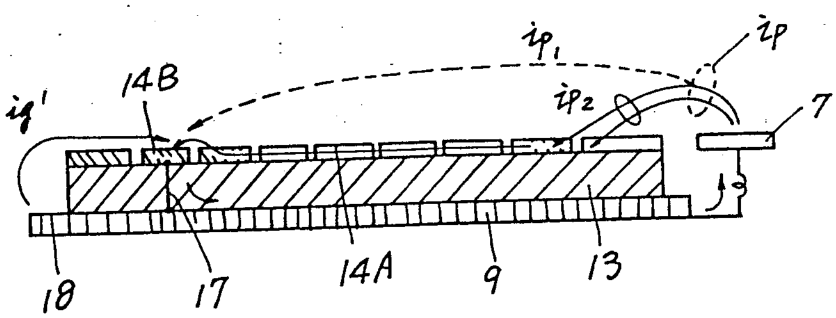

Fig. 8

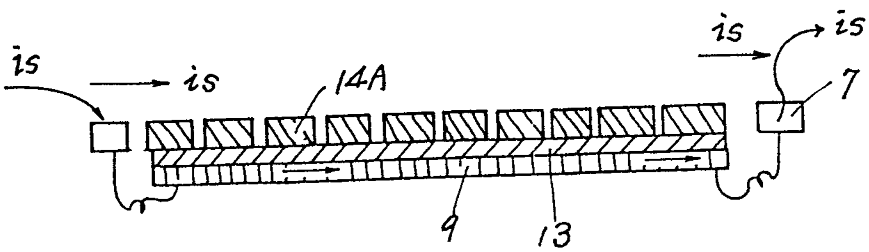

Fig. 9

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 83 11 2664

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	PATENTS ABSTRACTS OF JAPAN, vol. 7, no. 104 (M-212)[1249], 6th May 1983; & JP - A - 58 26 695 (MITSUBISHI JUKOGYO K.K.) 17-02-1983 * abstract * ---	1,2	B 63 B 59/04 C 23 F 13/00
X	PATENTS ABSTRACTS OF JAPAN, vol. 7, no. 128 (M-220)[1273], 3rd June 1983; & JP - A - 58 47 696 (MITSUBISHI JUKOGYO K.K.) 19-03-1983 * abstract * ---	1,2	
A	FR-A-2 256 072 (ZONDEK) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			B 63 B 59/04 C 23 F 13/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19-09-1984	VAN LEEUWEN R.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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