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(54) Title: IONOMER COATED ELECTRODE

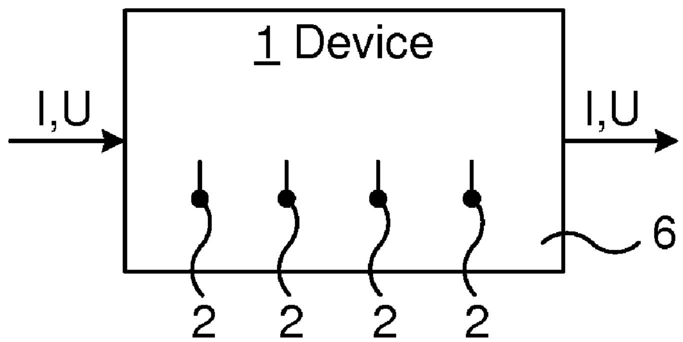

Fig. 1

(57) Abstract: The present application relates to a use of an ionomer coated electrode (2) for controlling electrical potential of a fluid (6) in a high-voltage device (1). It also relates to a fluid-filled high-voltage device e.g. a HVDC converter, (1) comprising a plurality of ionomer coated electrodes (2) for controlling electrical potential of the fluid (6). In a preferred embodiment, the electrode comprises a titanium or palladium core coated with NAFION as ionomer. Optionally, the titanium can be coated with an electrocatalytic layer comprising iridium oxide (lr2O3) or ruthenium oxide (RuO2).

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IONOMER COATED ELECTRODE

TECHNICAL FIELD

The present disclosure relates to controlling of electrical potential in a fluid-filled high-voltage device.

BACKGROUND

A high-voltage direct current (HVDC) converter valve may be air-insulated, water-cooled and suspended indoors in a controlled environment. The electrical potential in the cooling water is controlled by means of hundreds of electrodes for controlling (also called to grade) the potential of the water, and to take up leakage currents in the water, at the different points in the valve where the electrodes are positioned, thereby allowing the valve potentials to be adjusted to avoid dielectric failure (flash-over) in the cooling water, with possible water leakage as a result. The use of electrodes in high-voltage application is disclosed e.g. in US 4,470,007 which discusses the use of electrodes for testing the electrical breakdown resistance potential of insulating media and/or cooling media.

Since the environment in the cooling water is very harsh, with high DC and AC (alternating current) potentials, leakage currents, high temperature and the presence of reactive ions, the electrodes need a high resistance to corrosion, as discussed e.g. by P.O. Jackson *et al.* in "Corrosion in HVDC Valve Cooling Systems" IEEE Transactions on Power Delivery, Vol. 12, No. 2, April 1997, pages 1049-1052. Traditionally, platinum (Pt) electrodes are used since they are resistant to corrosion in such a harsh environment, but Pt electrodes are very expensive, especially considering the large amount of electrodes needed for controlling an HVDC valve. Pt electrodes are also susceptible to deposition of precipitated material from ions, e.g. aluminium (Al^{3+}) and hydroxide (OH^-) ions forming deposited $Al(OH)x$, inevitably present in the cooling water, which deposits reduce the efficiency of the electrodes since they are electrically insulating and increase the risk of flash-overs/partial discharges. This may lead to local dielectric phenomena which may induce e.g. seal or plastic water pipe leakage.

SUMMARY

It is an objective of the present invention to alleviate problems with the prior art electrodes while reducing the cost thereof.

It has now been found that an outer coating of an ionomer, e.g. Nafion, on an electrode used in a fluid-filled high-voltage device significantly reduces the amount of deposits on the electrode. It has also been found that much cheaper electrodes, based on palladium (Pd) or titanium (Ti) may be used instead of the more expensive Pt electrodes. These electrodes have shown surprisingly high resistance to corrosion when used in fluid-filled high-voltage devices. When using the Pd or Ti electrodes, preferably in combination with an outer ionomer coating for reduced deposition, electrodes which are comparable or improved with regard to life span compared with Pt electrodes, are achieved to a much lower cost.

According to an aspect of the present invention, there is provided a use of (or a method of using) an ionomer coated electrode for controlling electrical potential of a fluid in a high-voltage device.

According to another aspect of the present invention, there is provided a fluid-filled high-voltage device comprising a plurality of ionomer coated electrodes for controlling electrical potential of the fluid with which the device is filled.

According to another aspect of the present invention, there is provided a use of (or a method of using) a titanium electrode with an electrocatalytic coating, e.g. comprising mixed metal oxide or platinum group metal oxide, preferably iridium oxide (IrO_2) or ruthenium oxide (RuO_2), especially iridium oxide, for controlling electrical potential of a fluid in a high-voltage device. Alternatively, the coating may be platinum metal.

According to another aspect of the present invention, there is provided a use of (or a method of using) a palladium electrode for controlling electrical potential of a fluid in a high-voltage device.

It is to be noted that any feature of any of the aspects may be applied to any other aspect, wherever appropriate. Likewise, any advantage of any of the aspects may apply to any of the other aspects. Other objectives, features and advantages of the enclosed embodiments will be apparent from the following detailed disclosure, from the attached dependent claims as well as from the drawings.

Generally, all terms used in the claims are to be interpreted according to their ordinary meaning in the technical field, unless explicitly defined otherwise herein. All references to "a/an/the element, apparatus, component, means, step, etc." are to be interpreted openly as referring to at least one instance of the element, apparatus, component, means, step, etc., unless explicitly stated otherwise. The steps of any method disclosed herein do not have to be performed in the exact order disclosed, unless explicitly stated. The use of “first”, “second” etc. for different features/components of the present disclosure are only intended to distinguish the features/components from other similar features/components and not to impart any order or hierarchy to the features/components.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments will be described, by way of example, with reference to the accompanying drawings, in which:

Fig 1 is a schematic block diagram of an embodiment of a fluid-filled electrical device in accordance with the present invention.

Fig 2a is a schematic illustration in longitudinal section of an embodiment of an electrode in accordance with the present invention.

Fig 2b is a schematic illustration in longitudinal section of another embodiment of an electrode in accordance with the present invention.

Fig 2c is a schematic illustration in longitudinal section of another embodiment of an electrode in accordance with the present invention.

Fig 2d is a schematic illustration in longitudinal section of another embodiment of an electrode in accordance with the present invention.

DETAILED DESCRIPTION

Embodiments will now be described more fully hereinafter with reference to the accompanying drawings, in which certain embodiments are shown. However, other embodiments in many different forms are possible within the scope of the present disclosure. Rather, the following embodiments are provided by way of example so that this disclosure will be thorough and complete, and will fully convey the scope of the disclosure to those skilled in the art. Like numbers refer to like elements throughout the description.

An ionomer, as discussed herein, is a polymer composed of ionomer molecules, wherein ionomer molecules are macromolecules in which a small but significant proportion of the constitutional units have ionisable and/or ionic groups. Nafion is a commercially available ionomer.

Figure 1 is a schematic illustration of a high-voltage electrical device 1. A current (I) having a voltage (U) enters the device 1, and a, typically different, current (I) having a voltage (U) exits the device 1 as illustrated by the arrows and references I and U in the figure. The current may be AC or DC or a combination thereof, or some other periodic waveform such as a half period AC or distorted AC waveform. If the device 1 for instance is an HVDC converter valve, the currents within the valve 1 may be a mixture of AC and DC in different points of the valve, further increasing the general harshness of the environment therein.

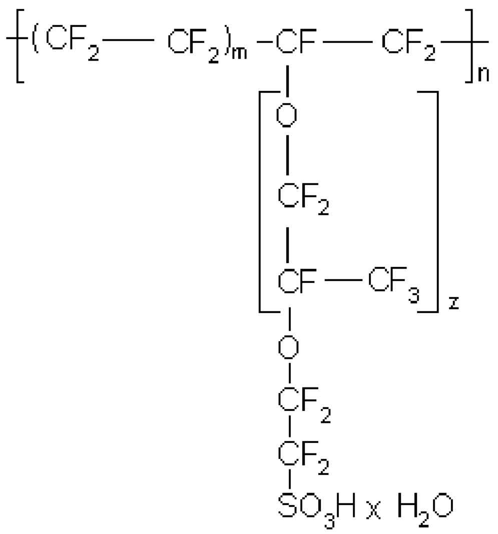
The device 1 is filled with a fluid for insulation and/or cooling of the device. In the example of the device 1 being an HVDC valve, the fluid is typically an aqueous cooling liquid such as essentially pure water or water mixed with glycol or other freeze-point lowering chemical to prevent the liquid from freezing in cold climate applications. However, any electrically insulating fluid e.g. an oil such as a mineral oil, or an ester liquid may be used.

The device comprises a plurality of electrodes 2 for controlling the electrical potential in the fluid at different points in the device 1. The number of electrodes 2 used may be high in e.g. an HVDC valve since the valve is a large structure (several meters long and across) and considering that it is used for three AC phases and the electrodes have two polarities (cathode and anode), although the same electrode may be used alternatingly as a cathode and as an anode depending on the circumstances. The number of electrodes 2 in the device 1 may e.g. be at least a hundred or at lest a thousand electrodes. Typically, the control system acts on a signal from a conductivity meter in the valve cooling system. The electrodes 2 are placed at such positions, some distance from the semiconductor heat sinks in the cooling system, that the potentials at these points will not be too high or low. Thereby, the potential in the cooling fluid 6 is controlled by means of the electrodes by designing the cooling system with the electrodes to achieve proper distribution of electrical potential and not too high leakage currents at any point in the cooling system.

Figure 2a illustrates an embodiment of an electrode 2 which may be used in a high-voltage device 1 in accordance with the present invention. The electrode 2 comprises a core 3 which is not coated, e.g. a solid (non-hollow) rod-shaped core 3. The core may be of, essentially pure, palladium which has shown great resistance to corrosion even without a coating. Palladium electrodes as such are well known but not for the use in a high-voltage electrical device 1 as per the present invention.

Figure 2b illustrates another embodiment of an electrode 2 which may be used in a high-voltage device 1 in accordance with the present invention. The electrode 2 comprises a core 3 which is coated, e.g. a solid (non-hollow) rod-shaped core 3. The coating 4 may be an oxide coating, e.g. an iridium or ruthenium oxide coating, for protecting the core 3 from corrosion. The core may be of, essentially pure titanium which has shown great resistance to corrosion with a coating 4 of preferably iridium oxide. Titanium electrodes coated with iridium oxide are known as such, e.g. from US 3,711,385 or US 3,878,083, but not for the use in a high-voltage electrical device 1 as per the present invention.

Figure 2c illustrates another embodiment of an electrode 2 which may be used in a high-voltage device 1 in accordance with the present invention. The electrode 2 comprises a core 3 which is coated, e.g. a solid (non-hollow) rod-shaped core 3. The core may be of, essentially pure, palladium or titanium, preferably palladium which does not need an oxide coating. The core 3 is instead coated by means of an ionomer coating 5. An ionomer coating 5 has been shown to reduce the deposition of electrically insulating material on the electrode, increasing the life span and efficiency of the electrode. The ionomer may e.g. be Nafion which may be defined with the following molecular structure:

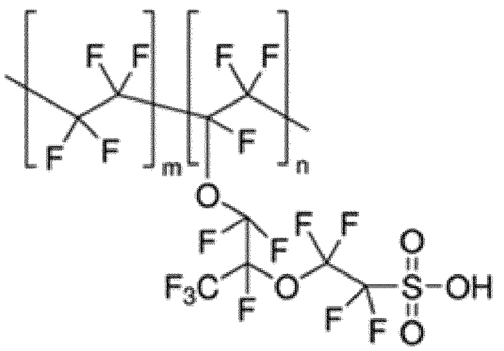


m: 5 - 13.5

n: ca. 1000

z: 1,2,3 ...

, for example Nafion having the following molecular structure:



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which is commercially available (CAS number 31175-20-9) as a perfluorinated ion exchange resin solution, for example with an approximate equivalent weight (EW) of 1100 (i.e. Nafion EW1100). The electrode 2 may be coated with the ionomer e.g. by dipping the electrode (or rather, the core 3 of the electrode) into the ionomer solution and allowing it to dry in air, possibly heated air. The ionomer coating may then get a thickness of 5-5000 nanometres (nm), e.g. 100-1000 nm such as 300-600 nm.

Figure 2d illustrates another embodiment of an electrode 2 which may be used in a high-voltage device 1 in accordance with the present invention. The electrode 2 comprises a core 3 which is coated, e.g. a solid (non-hollow) rod-shaped core 3. The coating 4 may be an oxide coating, e.g. an iridium oxide coating, for protecting the core 3 from corrosion. The core may be of, essentially pure, palladium or titanium, preferably titanium which has shown great resistance to corrosion especially with a coating 4 of preferably iridium oxide. The coated electrode is then provided with a second (outer) ionomer coating in the same way as discussed with reference to figure 2c.

Different embodiments of the electrode 2 have above been discussed with reference to the figures 2a-d, but other electrode structures are also possible within the scope of the present invention. For instance, any number of coatings may be used, e.g. depending on the core 3 material used. If an ionomer coating 5 is used, this coating is preferably an outermost coating in order to better protect the electrode 2 from deposition. It is also noted that the core 3 may be of other materials, elemental or alloys, than Pd and Ti, e.g. Nb (niobium) or Ta (tantalum), and that the core 3 may alternatively be hollow.

The electrodes 2 may be of any suitable shape, depending on the application, but may typically be rod-shaped, e.g. having a diameter of 1-3 mm, e.g. about 2 mm, and/or a length of 20-80 mm.

As discussed herein, the environment in the high-voltage device may be harsh and corrosive, and below some aspects of this harsh environment are further discussed.

The electrodes 2 are typically at (or connected to) different, but high, electrical potentials within the device 1, which also leads to high leakage currents. Each or at least some of the electrodes may be at an electrical potential of between 100 and 800 kV. However, at least some electrodes may also be at potentials lower than 100 kV or be grounded.

As regards the leakage current in e.g. HVDC valve applications, the leakage current density at an electrode 2 may preferably be below 3.4 A/m^2, which corresponds to approximately 0.5 mA at a rod shaped electrode. Thus, the electrodes 2 may be exposed to (and collect/take up) high leakage currents, such as leakage currents of at least 0.1 mA, e.g. at least 0.2 or 0.4 mA, although lower currents may additionally or alternatively occur. It should be noted that the electrodes may have any suitable shape, not necessarily a rod shape, such as a tubular, ring shaped or plate shape.

The temperature of the fluid 6 may e.g. be between -10 and 70°C. Temperature fluctuations between 10 and 70°C under operation, as well as a high temperature of between 50 and 70°C which occur in some embodiments of the present invention, may increase the strain on the electrodes and the corrosivity of the environment.

Even if deionized water is used for the fluid 6, ions may inevitably be present in the fluid 6. Also, if the device 1 is used in a cold climate, glycol (e.g. ethylene glycol) may be comprised in the fluid 6 to prevent it from freezing if the fluid temperature is below zero degrees Celsius. The ions in the fluid may e.g. comprise chloride, magnesium, hydrogen carbonate and/or calcium ions.

The possible combination of AC and DC currents, possibly fluctuating also increases the strain on the electrodes.

The electrical field which is distributed between two rod shaped electrodes 2 in a device 1 filled with fluid 6, e.g. deionized water. For example, a voltage of 36 kV over a distance of 2.1 m will result in a maximum electric field of approximately 75 kV/m close to the electrode 2 (this value should be compared with the average electric field 36/2.1 = 17 kV/m.)

The present disclosure has mainly been described above with reference to a few embodiments. However, as is readily appreciated by a person skilled in the art, other embodiments than the ones disclosed above are equally possible within the scope of the present disclosure, as defined by the appended claims.

CLAIMS

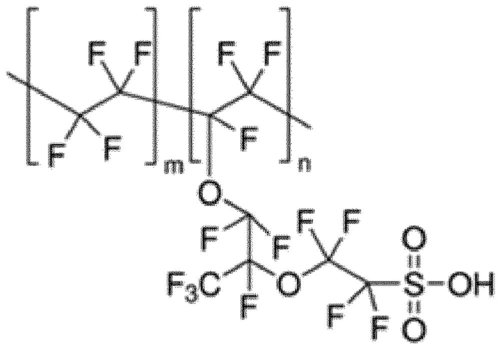
1. Use of an ionomer coated electrode (2) for controlling electrical potential of a fluid (6) in a high-voltage electrical device (1).

2. The use of claim 1, wherein the electrode (2) is an ionomer coated titanium or palladium electrode.

3. The use of claim 2, wherein the electrode (2) is an ionomer coated titanium electrode with an intermediate coating (4) which comprises iridium oxide as a major component.

4. The use of any preceding claim, wherein the ionomer (5) is Nafion.

5. The use of claim 4, wherein the Nafion (5) has the following molecular structure:



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6. The use of any preceding claim, wherein the ionomer coating (5) has a thickness of 5-5000 nm, e.g. 100-1000 nm such as 300-600 nm.

7. The use of any preceding claim, wherein the fluid (6) is an aqueous cooling liquid, e.g. essentially pure deionized water or deionized water admixed with glycol.

8. The use of any preceding claim, wherein the device (1) is an HVDC converter valve.

9. The use of any preceding claim, wherein the electrode (2) is at an electrical potential of 100-800 kV.

10. The use of any preceding claim, wherein the electrode (2) is exposed to leakage currents of at least 0.1 mA, e.g. at least 0.2 or 0.4 mA.

11. The use of any preceding claim, wherein the fluid (6) has a temperature of 50-70°C.

12. The use of any preceding claim, wherein the electrode (2) is used as both an anode and a cathode for controlling the electrical potential.

13. The use of any preceding claim, wherein the electrode (2) is rod-shaped.

14. A fluid-filled high-voltage device (1) comprising a plurality of ionomer coated electrodes (2) for controlling electrical potential of the fluid (6).

15. The device of claim 14, comprising at least 100, e.g. at least 1000, of the ionomer coated electrodes (2).

16. The device of claim 14 or 15, wherein the device (1) is an HVDC converter valve.

17. Use of a titanium electrode (2) coated with an electrocatalytic coating (4) comprising iridium oxide or ruthenium oxide, for controlling electrical potential of a fluid (6) in a high-voltage device (1).

18. Use of a palladium electrode (2) for controlling electrical potential of a fluid (6) in a high-voltage device (1).

19. The use of claim 18 or 19, wherein the electrode (2) has an outer ionomer coating (5), e.g. a Nafion coating.

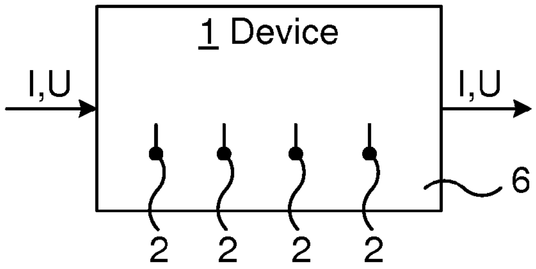

Fig. 1

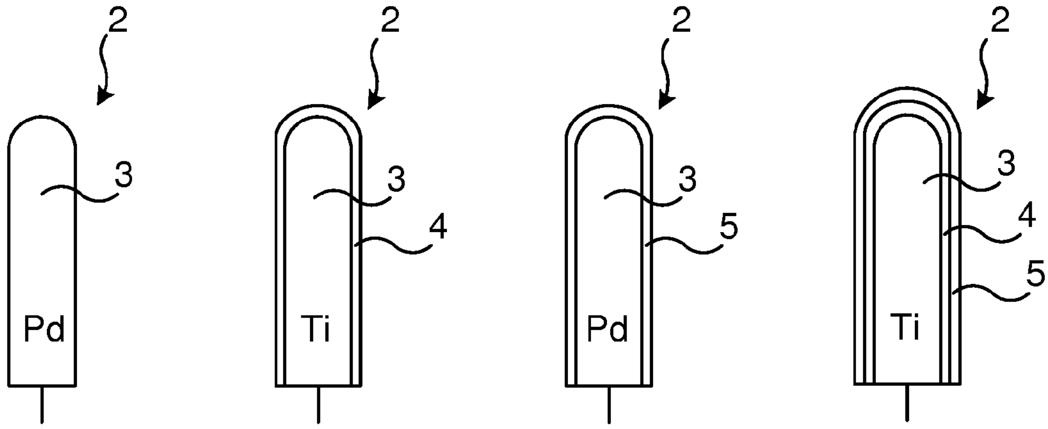

Fig. 2a Fig. 2b Fig. 2c Fig. 2d

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/050621

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N27/416 H02M1/32
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N H02M H02J H01M

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2007 082288 A (TOSHIBA CORP) 29 March 2007 (2007-03-29)	1,8-16
Y	abstract	4-6
A	paragraph [0019] paragraph [0024] - paragraph [0040] figures	17-19
Y	US 6 867 159 B2 (EBBRELL GUY [CA] ET AL) 15 March 2005 (2005-03-15)	4-6
A	column 6, line 5 - column 8, line 56	1,19
X	DE 196 00 207 A1 (PERMASCAND AB [SE]) 5 September 1996 (1996-09-05)	1,2,4, 12-15
Y	column 3, line 13 - column 5, line 68 figures	3,7-11, 16-19

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

[X] See patent family annex.

* Special categories of cited documents :

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

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 June 2015	03/07/2015

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

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/050621

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 711 385 A (BEER H) 16 January 1973 (1973-01-16) cited in the application column 2, line 21 - column 4, line 68 examples -----	3,17-19
Y	LIPS H P: "Water cooling of HVDC thyristor valves", IEEE TRANSACTIONS ON POWER DELIVERY, vol. 9, no. 4, 1994, pages 1830-1837, XP055196899, ISSN: 0885-8977, DOI: 10.1109/61.329516	7-11,16
A	page 1831, left-hand column, paragraph 2 - page 1834, left-hand column, paragraph 1 -----	12-14
A	TYKESON K ET AL: "Environmental and geographical aspects in HVdc electrode design", IEEE TRANSACTIONS ON POWER DELIVERY, vol. 11, no. 4, October 1996 (1996-10), pages 1948-1954, XP011049261, ISSN: 0885-8977, DOI: 10.1109/61.544281 page 1949, left-hand column, paragraph 4 - page 1951, left-hand column, paragraph 4 -----	1-3,12, 13,17,18

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/050621

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
JP 2007082288	A	29-03-2007	NONE			
US 6867159	B2	15-03-2005	CA	2452041	A1	04-06-2004
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			NO	960011	A	05-07-1996
US 3711385	A	16-01-1973	US	3711385	A	16-01-1973
			US	3864163	A	04-02-1975