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(54) Electrical circuit interruption device.

(57) An electrical circuit interruption device (fuse) having an inherently conductive polymer, preferably a polypyrrole, as its actuating element. Such fuses (A) "blow" substantially faster than conventional metal fuses (B) at low overload currents. Oxidising dopants such as perchlorate or picrate ions may be used to enhance the circuit-breaking effect, and the fuses, whether or not so doped, may advantageously be used as electrical primers ("bridge wires") for pyrotechnic devices.

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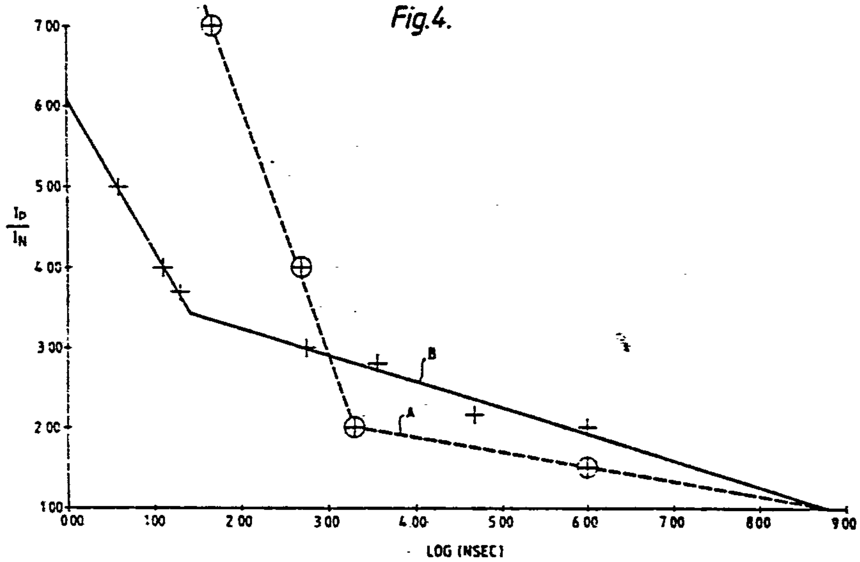
Fig.4.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This invention relates to devices for the interruption of electrical circuits.

A known form of electrical circuit interruption device is the conventional metallic fuse which may be designed to operate at various current ratings but is generally unsatisfactory at low operating currents because it either takes a relatively long time to "blow" at moderate overloads or, if it is a "quick-blow" fuse, then its life-time at the rated current is relatively short - often a matter of only a few hours. This slowness of actuation is a particular problem in electronic equipment such as integrated circuits where moderate overload currents can be tolerated in operation for only very short intervals, and the short life-time of the "quick-blow" fuse is obviously inconvenient.

The present invention provides an electrical circuit interruption device having an actuating element comprising an inherently electrically conductive polymer.

Inherently electrically conductive polymers (hereinafter "conductive polymers") can be selected which have a conductivity high enough to pass a substantial current, and can thus serve as the actuating element of the device according to the present invention. These polymers are highly advantageous for use as the actuating element in circuit protection devices, such as fuses, especially at low operating currents, by which is meant less than 1 Amp, preferably less than 200mA, more preferably less than 100mA, and especially less that 50mA. It has been found that at moderate to low overload currents, the time taken for the conductive polymer actuating element to "blow" (that is, to interrupt the circuit) is considerably shorter than found in conventional fuses of comparable life-time at the rated current of the device. It will be understood that the circuit interruption may be effected by reduction of the current to a negligible level e.g. by increasing the resistance of the actuating element, without physically destroying or breaking the actuating element. However, physical breakage or destruction is preferred. Preferably the conductive polymer is selected and arranged so that the actuating element takes less than 60 seconds to interrupt the circuit when carrying twice the rated operating current, and is capable of continuously carrying its rated operating current for at least 24 hours. For example, a 50mA rated device according to the present invention has been found to "blow" in 2 to 3 seconds at a current of 100mA (i.e. twice the rated current) whereas a conventional metal 50mA rated fuse continued to pass a 100mA current for about 17 minutes before "blowing".

Known electrically conductive polymers include polysulphur nitrides, polyanilines, polyphenylenes, polyacetylenes and polypyrroles. Although some polymers, e.g. ((SN)x, are intrinsically conductive, many polymers require oxidation (or reduction) to render them significantly electrically conductive. For example, polyacetylenes require oxidation or reduction, polypyrroles require oxidation. The process of oxidation (or reduction) is often called doping and a counter ion is required to associate itself with the (or reduced) polymer to balance the ionic charges therein. This counter-ion is often referred to as a dopant. Examples of dopants include BF_4^-, p-toluene sulphonate, Br^-, perchlorate ions, picrate ions and positively charged ions such as alkyl ammonium ions and metal ions such as potassium ions.

Polyacetylenes may be prepared as described by H. Shirakawa et al, J. Polymer Sci., Polym. Chem. Ed., 12, 11 (1974); polyphenylenes may be prepared as described by J.K. Stille et al, J. Polymer Sci, Part D, 5, 385 (1971); polyanilines, polynaphthylamines and polythiophenes may be prepared by methods analogous to the polypyrrole preparations described below.

In the interests of clarity, the phrase "electrically conductive polymer" will be used herein to mean any polymer or oligomer inherently capable of electrical conductivity or semi-conductivity, (hereinafter both included in the terms "electrical conductivity" or "electrically conductive"), including those requiring oxidation/reduction of the polymer and/or the presence of a "dopant" to render them electrically conductive. Thus, the aforesaid phrase includes inorganic polymers such as the polysulphur nitrides, and organic polymers such as the polypyrroles, all of which conduct electronically, electronic conduction being preferred for the present purposes. The phrase excludes single-element substances such as carbon, silicon, germanium.

The terms "doping" and "de-doping" will be taken to mean the oxidation/reduction processes used to convert the polymers between their less conductive and more conductive states; the term "dopants" will refer to the aforementioned counter-ions and to the materials used to provide the counter-ions which stabilise the more conductive form of the polymers; and the terms "undoped", "doped" and "de-doped" will be understood accordingly.

The preferred conductive polymers for use in the present invention are polypyrrole and its suitably conductive derivatives, e.g. poly(3,4-dimethylpyrrole). These polymers in their doped conductive state have the necessary resistance to degradation on aging, and can be synthesised in suitable physical forms.

Polypyrrole and suitably substituted derivatives may be prepared from pyrroles as shown by the accompanying general formula (I) in Fig. 1 of the accompanying drawings, in which R_1 to R_5, which may be the same or different, represent possible substituents, although sufficient positions must be left unsubstituted to permit polymerisation. Electrically conductive polymers are generally believed to operate by means of a conjugated pi-electron system and it is understood that some substituents or combinations of substituents may interfere with the conjugated system so as to detract from or destroy the desired electrical conductivity. Acceptable substituents can be readily determined by simply testing the conductivity of the resulting polymer.

Electrochemical methods of preparing electrically conductive polymers can be used as follows to produce the actuating element materials of the present invention. In general, an electrochemical cell is used, wherein two electrodes (made from, for example, stainless steel, platinum or indium oxide coated glass) are immersed in an electrolyte mixture, suspension or solution. The electrolyte includes a material carrying groups which are ionisable into an appropriately charged ionic dopant species. The solvent or mixture of solvents may be chosen from protic and aprotic solvents, for example acetonitrile, tetrahydrofuran, dimethyl formamide, water, methanol. To the electrolyte mixture is added the monomer species that is to be polymerised to form the desired electrically conductive polymer. Stirring of the resulting mixture may be required to achieve a homogeneous mixture. Upon operation of the cell, an electrically conducting film is formed on the appropriate electrode. With positively charged polymers such as polypyrroles, the film is formed on the anode and is partially oxidised and contains a negatively charged dopant to provide charge neutrality to the film.

Chemical preparative methods can also be used, in which the monomer and the dopant are mixed with an oxidising agent in a suitable liquid vehicle.

Some specific examples of the preparation of various conductive polymers suitable for use as the actuating element of the present invention will now be described.

Preparation 1

Two stainless steel electrodes 2cm apart were employed as the anode and cathode of an electrolytic cell, having an electrolyte mixture consisting of 0.1M commercially available $LiBF_4$ in 50 ccs acetonitrile, together with 0.06 moles of pyrrole. During the operation of the cell the mixture was stirred.

The electrolytic cell was powered by a D.C. power supply. Electrolysis of the electrolyte mixture was carried out by applying to the cell an electrical potential of 5V for a period of one hour, during which time the current density was $1mAcm^{-2}$.

A brittle black film was deposited on the anode and was removed with difficulty to give a free-standing film, which could not be creased or folded in two like paper without fracturing.

Preparation 2

A similar procedure to that of Preparation 1 was followed but this time employing as the electrolyte a 0.1M solution of sodium p-toluenesulphonate in 75cc acetonitrile. The cell was operated at a current density of $1mAcm^{-2}$ for 45 minutes. A black free standing flexible film was obtained.

Preparation 3

130 cm^3 of polyethylene glycol (MW=200), 130 cm^3 of 0.1M tetrabutylammonium perchlorate in aceto-

nitrile, and 7 cm^3 of pyrrole were subjected to electrolysis under stirring at a current density of about 1mAcm^{-2} using a stainless steel gauze cathode.

A flexible film of polypyrrole doped with perchlorate ions and incorporating polyethylene glycol was produced, the polyethylene glycol acting as a "fuel" for destructive oxidation (detonation) by the perchlorate ions under conditions of use described hereinafter.

Preparation 4

130 cm^3 of 0.1M picric acid in acetonitrile, 10 cc's of water, and 7 cm^3 of pyrrole were subjected to electrolysis as in Preparation 3. A black flexible film of polypyrrole doped with picrate ions was produced, the picrate undergoing detonation when sufficient current was passed through the polymer in use as hereinafter described.

Self-supporting, preferably flexible, films of the conductive polymer may be advantageously used as the actuating element, although rigid films and films supported on suitable carriers are not excluded.

Preferred polypyrrole derivatives and dopants include polypyrrole doped with chloride, fluoroborate, perchlorate, or p-toluene sulphonate ions, the last of these dopants tending to produce more flexible films.

The invention also provides a method of protecting an electrical circuit comprising incorporating in the circuit a circuit interruption device of the present kind.

Devices according to the present invention may be conveniently incorporated into electrical circuitry, for example in printed circuit boards, if desired in combination with other protective devices.

The actuating element of the present invention may be enclosed in suitable preservative environments for example in vacuum or nitrogen gas or in a "potting" compound or electrically insulating oils if necessary, e.g. to minimise oxidation. This would be highly desirable for readily oxidised polymers such as polyacetylenes, and is preferable for polypyrroles.

By way of example to illustrate the present invention an electrical circuit interruption device will be described schematically with reference to Fig. 2 and 3 of the accompanying drawings in which,

(1) is the conductive polymer actuating element comprising a strip of conductive polymer,

(2) is the middle section of the device,

(3) is a conductive part attaching the actuating element to the circuit, and

(4) is a load in the circuit.

There are two modes by which the device of the present invention may "blow":-

Mode 1: When the overload current is relatively small, e.g. twice the rated current, the resistivity of the polymer increases in an area (3) towards the middle of the actuating element. Hence the current passing through the actuating element is substantially reduced and so the electrical equipment is protected.

Mode 2: At a higher initial level of overload current, "blowing" occurs by actual physical destruction of the actuating element.

These two modes of actuation do not necessarily exclude each other as Mode 2 may occur after Mode 1 if the applied voltage is increased to a sufficiently high level.

A specific shape and arrangement of a device according to the invention are shown in Fig. 3 of the accompanying drawings. It will be appreciated that the dimensions and configuration of the conductive polymer actuating element may be selected to suit the inherent electrical resistivity of the polymer in order to produce a circuit interruption device of desired rating and overload performance. The dimensions and shape of the actuating element are thus not critical in themselves, but dimensions substantially as shown in Fig.3, with the conductivity of the polymer in the range from 10 to 500 $\text{ohms}^{-1}\text{cm}^{-1}$, have been found convenient in practice.

The invention will now be further illustrated by the following specific examples in which electrical conductivity is measured by a 4-probe method similar to that described in "Organic Semiconducting Polymers", Ed. J.E. Katon (Marcel Dekker 1968).

Example 1

A fuse as shown in Fig. 3 rated at 50 - 60 mA was prepared with an actuating element (1) comprising a strip of electrochemically prepared (see Preparation 2) polypyrrole doped with p-toluenesulphonate ions and having the dimensions indicated in Fig. 3, and a conductivity of 100 ohms^{-1}cm^{-1}.

The times taken for the device to "blow" were tested and these results are shown in graph A of Fig. 4 of the drawings in which the relative amount of overload current over rated current is plotted againt the logarithm of the time taken to "blow", and compared with a similar graph B for a conventional 50 - 60mA rated metal fuse. From Fig. 4 it can be seen that the fuse according to the present example "blows" at a faster rate that the conventional fuse when subjected to overload currents of up to 3 times the rated current, and is very significantly faster at 1-1/2 to 2 times rated current. The fuse according to the present invention could if desired be combined with conventional fuses. It is an advantage of devices according to the present invention that their failure temperature is significantly lower than that of comparable conventional fuses, and in many cases the equilibrium running temperature may also be lower.

Example 2

A fuse was prepared as in Example 1 using BF_4-doped polypyrrole prepared as in Preparation 1, having a conductivity of 11 $ohm^{-1}cm^{-1}$. At a current of 120 mA, the fuse "blew" by reducing the current to a negligible level in 225 milliseconds.

In a further embodiment of the present invention the actuating element may carry materials which react chemically to enhance its circuit breaking function under overload currents. Materials which act to speed up the degradation or destruction of the actuating element under overload currents are especially useful, for example small amounts of substances which oxidise very rapidly on heating or passage of overload electric current through the conductive polymer actuating element so as to destroy it and break the circuit more rapidly. The oxidising substance could be carried simply as a coating in a restricted area on the actuating element for oxidation on heating thereof, but it is possible in accordance with the present invention for doped systems to carry an explosive dopant, such as picrate ions, or a rapidly oxidising dopant such as perchlorate ions, preferably in the presence of a suitable "fuel" as described in Preparation 3 and 4 above capable of explosive reaction with the dopant, thus conveniently combining the functions of doping and oxidation. A suitable fuel for the perchlorate dopant could be any readily oxidisable material which can be suitably associated with the perchlorate ions in or on the conductive polymer to produce the desired effect. Conveniently, the film itself may provide adequate fuel for the oxidation.

The circuit interruption device of this invention, whether or not itself rendered capable of rapid oxidation as aforesaid, may be used as an electrical initiator or primer for explosive devices, e.g. a so-called "bridge wire", in which the relatively fast response of the present device at low overload currents may provide better control of detonation.

Examples of rapidly oxidising devices follow.

Example 3

A fuse was prepared as in Example 1 using perchlorate/polyethylene glycol doped polypyrrole prepared as in Preparation 3, having a conductivity of 200 ohm^{-1}cm^{-1}. At a current of 120mA the fuse "blew" by detonation in 150 milliseconds.

Example 4

Example 1 was repeated using picrate-doped polypyrrole prepared as in Preparation 4, having a conductivity of 11 ohm^{-1}cm^{-1}. At a current of 120 mA the fuse "blew" by detonation in 1.1 seconds.

Claims

1. An electrical circuit interruption device having an actuating element comprising an inherently electrically conductive polymer.

2. A device according to Claim 1, wherein the conductive polymer is selected and arranged so that the actuating element takes less than 60 seconds to interrupt the circuit when carrying twice the rated operating current, and is capable of continuously carrying its rated operating current for at least 24 hours.

3. A device according to Claim 2 having a rated operating current below 1 Amp, preferably below 200mA and more preferably below 100mA.

4. A device according to Claim 1, 2 or 3, wherein the actuating element is a film substantially 15 mm long, 1 mm wide and 50 microns thick, and has a conductivity within the range from 10 to 500 $\text{ohms}^{-1}\text{cm}^{-1}$.

5. A device according to any one of the preceding claims, wherein the actuating element is a self-supporting film of the electrically conductive polymer.

6. A device according to any one of Claims 1 to 4, wherein the actuating element is carried on a support.

7. A device according to any of the preceding claims, wherein the actuating element carries materials which react chemically to enhance its circuit-breaking function under overload currents.

8. A device according to claim 7, wherein the actuating element carries material(s) capable of rapid oxidation upon passage of overload currents through the actuating element.

9. A device according to claim 8, wherein the conductive polymer of the actuating element is doped with an explosive dopant.

10. A device according to claim 9, wherein the dopant comprises picrate ions.

11. A device according to claim 8, wherein the conductive polymer of the actuating element is doped with a rapidly oxidising dopant.

12. A device according to claim 11, wherein the actuating element carries additional material capable of explosive reaction with the oxidising dopant.

13. A device according to claim 12, wherein the said additional material is a polymer, preferably polyethylene glycol, which is readily oxidisable by the dopant under overload conditions.

14. A device according to claim 11, 12 or 13, wherein the dopant comprises perchlorate ions.

15. A device according to any of the preceding claims, wherein the conductive polymer is a polymer or oligomer of pyrrole or a substituted pyrrole.

16. A device according to any of the preceding claims, wherein at least the said actuating element is enclosed in a preservative environment.

17. A device according to any of the preceding claims in combination with a second circuit protection device.

18. An electrical circuit incorporating a device according to any of the preceding Claims 1 to 17.

19. A pyrotechnic or explosive device incorporating in its actuating mechanism a device according to any of Claims 1 to 17.

Fig. 1.

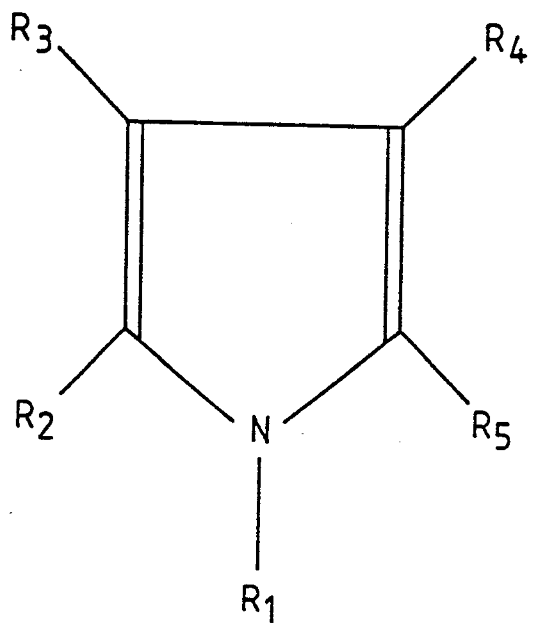

Fig. 2.

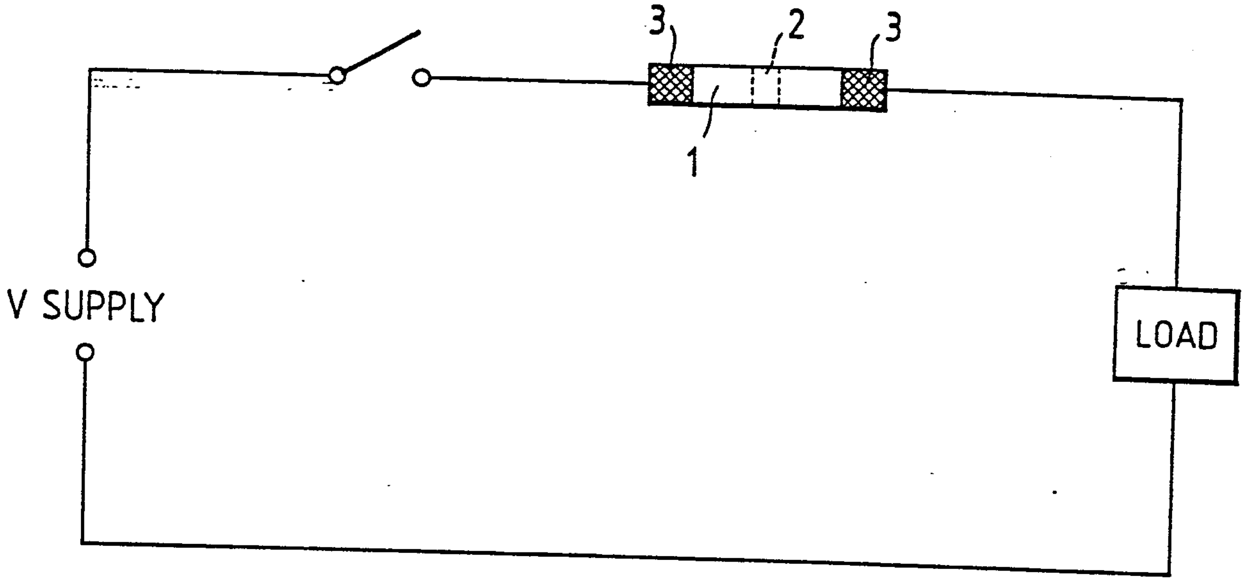

Fig. 3.

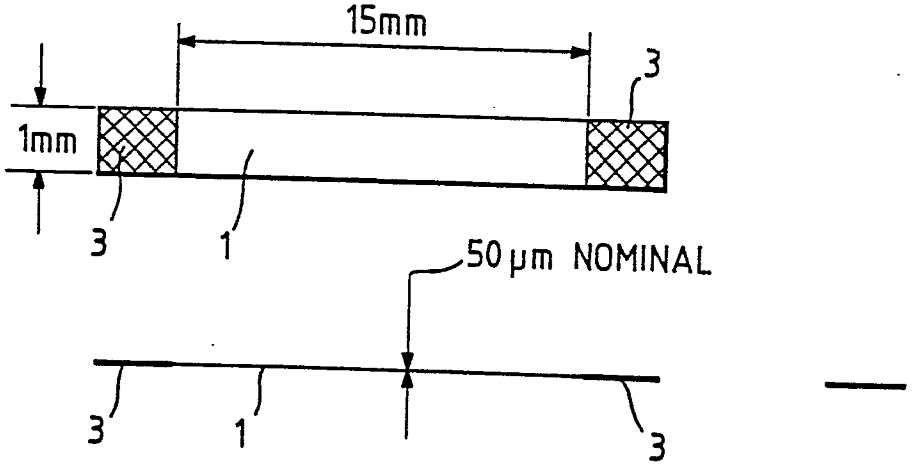

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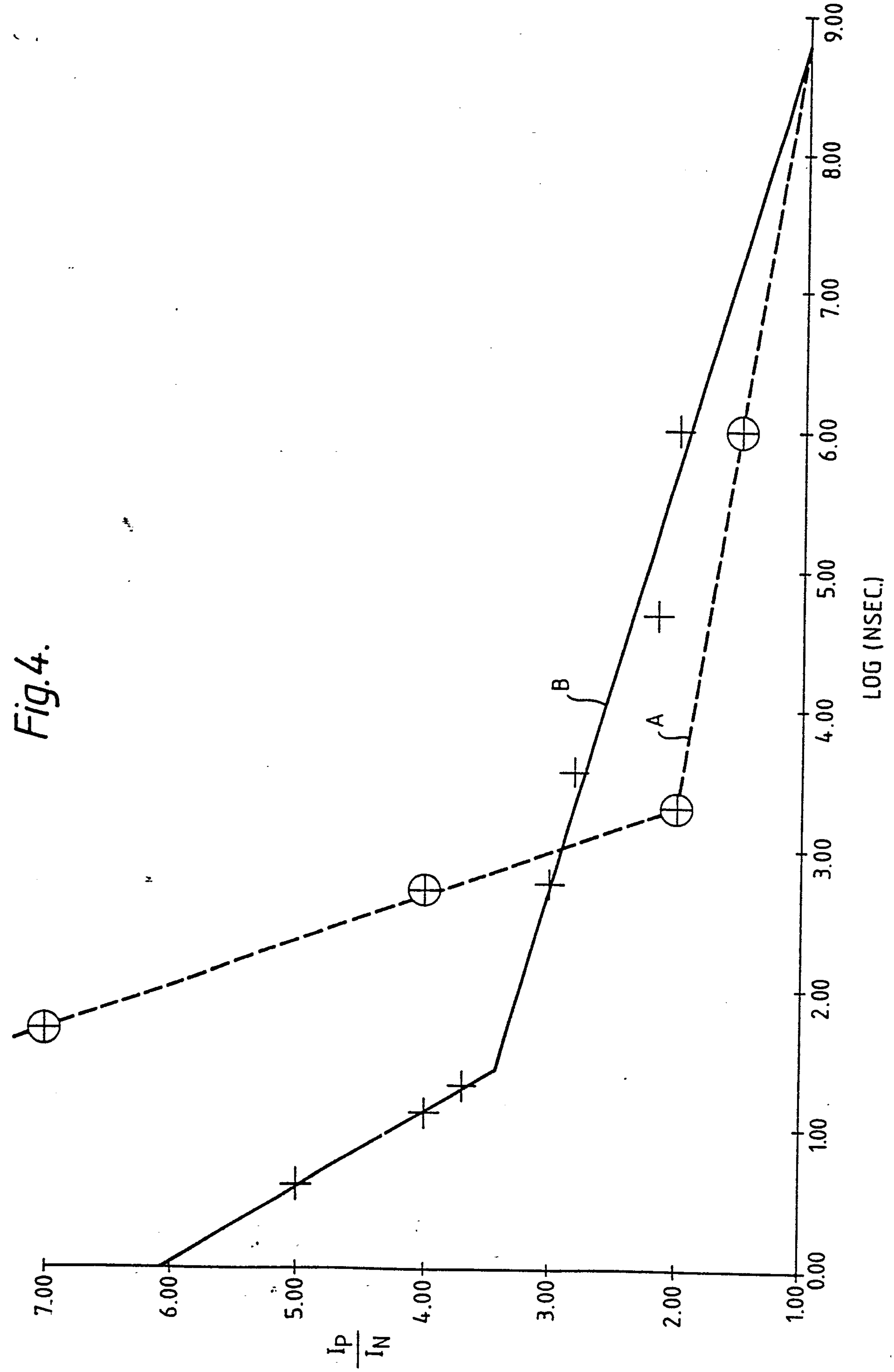
Fig.4.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EUROPEAN SEARCH REPORT

0115191

Application number

EP 83 30 7922

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)
A	US-A-4 293 836 (H. ARIKAWA) * Column 1, lines 5-61 * ---	1	H 01 H 85/04
A	EP-A-0 054 420 (MATSUSHITA ELECTRICAL INDUSTRIAL CO. LTD.) * Abstract; page 1 - page 2, paragraph 1 * ---	1	
A	EP-A-0 059 342 (BASF AG) * Abstract * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			H 01 H 85/00 H 01 B 1/12 H 01 L 29/28

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	08-03-1984	RUPPERT W

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