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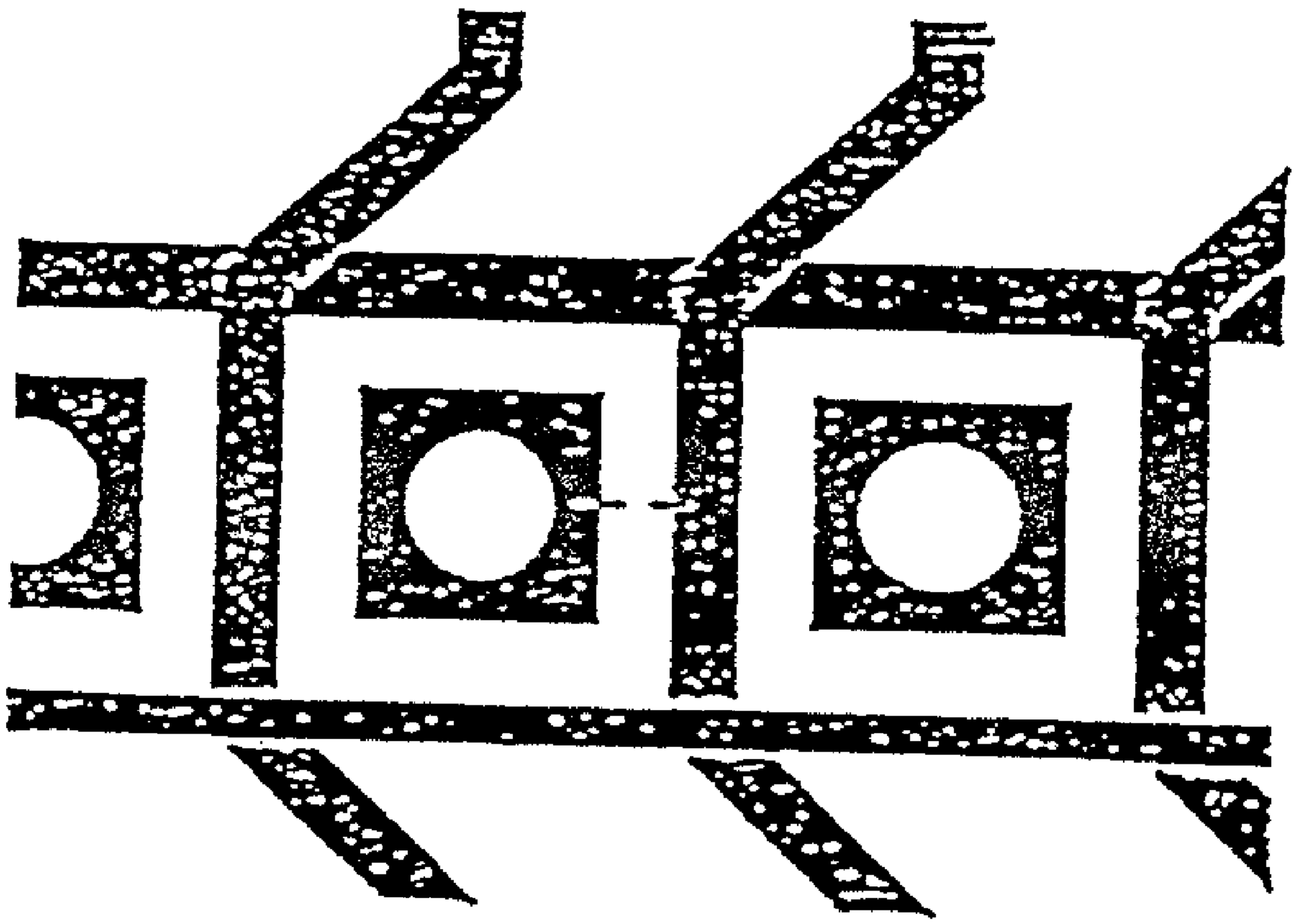
(54) Titre : CIRCUITS IMPRIMES EN POLYALKYLENDIOXYTHIOPHENE
(54) Title: PRINTED CONDUCTORS MADE OF POLYALKYLENE DIOXYTHIOPHENE



(57) Abrégé/Abstract:
The invention relates to a process for coating substrates, such as paper or plastic films, with open, electrically conductive structures, by ink-jet printing. A polymer solution made from water-dispersible polyalkylenedioxythiophenes is used for the printing process.

Conductor tracks made from polyalkylenedioxythiophenes

Abstract

The invention relates to a process for coating substrates, such as paper or plastic films, with open, electrically conductive structures, by ink-jet printing. A polymer solution made from water-dispersible polyalkylenedioxythiophenes is used for the printing process.

PRINTED CONDUCTORS MADE OF POLYALKYLENE DIOXYTHIOPHENE

The invention relates to a process for coating substrates, such as paper or plastic films, with open, electrically conductive structures, by ink-jet printing or using X,Y plotters. A polymer solution made from water-dispersible polyalkylenedioxythiophenes is used for the printing process.

Printed circuit boards used for electrical circuitry are well known substrates which have an electrically conductive structure. Printed circuit boards are composed of a rigid or flexible plastic substrate to which conductor tracks made from copper have been applied. The copper tracks are applied by photographic printing or by screen printing.

In photographic printing by the positive process the first step is full-surface application of copper to the substrate. Photoresist is distributed over the full surface of the copper. The photoresist is irradiated through a mask at those locations where conductor tracks are to run. The irradiation cures the photoresist. Subsequent development removes the uncured photoresist areas. The copper which is now uncovered is removed by etching in the next step. Once the cured photoresist has been removed (stripped) it is only the desired copper conductor tracks which remain.

In the screen printing process an image of the desired conductor structure is printed as an etch resist, onto a substrate with a full-surface covering of copper. In the etching which follows the copper between the desired conductor tracks is removed by etching, and then the etch resist is removed.

In the direct coating of a metal deposit onto nonconducting substrates there can be problems with the adhesion of the metal to the substrate. In this case a screen-printed paste based on an electrically conductive polymer can produce a good bond between substrate and superimposed layer. The conductor track structures made from the polymer are, for example, printed using screen printing onto a nonconducting substrate and then coppered chemically (DE 36 25 587, DE 36 27 256).

The use of electrically conductive polymers as an electrically conductive structure on substrates is also known in connection with polymer-based electroluminescence indicators (Science, 17 October 1997, p. 383). To apply the electrically conductive polymers, a solution of the polymers was introduced into the cartridge of an ink-jet

printer, and printed onto the substrate by the printer. A major problem with this process was that the organic solvent for the polymers, generally a halogenated hydrocarbon or tetrahydrofuran, attacked the plastic of the printer cartridge by salvation or swelling.

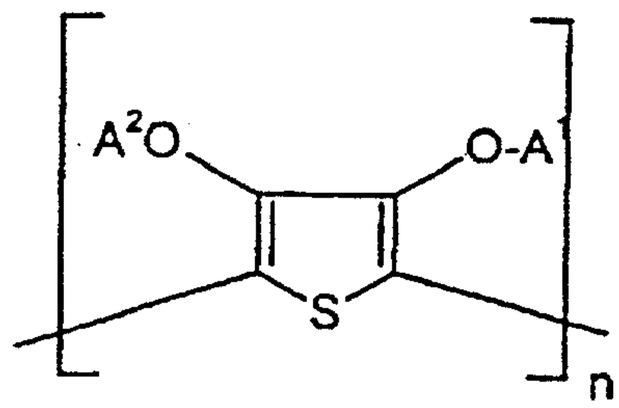
To avoid this disadvantage Y. Yang and J. Bharathan (Science, Vol. 279, 20 February 1998) used a water-soluble polymer from the polythiophene class of compounds. These water-soluble polymers did not attack the printer cartridges. Since structures of water-soluble polymers are also altered by atmospheric moisture, they are suitable only if they have no further contact with water after the water has been removed in an annealing step. In polymer-based luminescence indicators this condition poses no problem, since, after the water has been removed and after any further operations which may be required, conductive structures are encapsulated under inert conditions excluding water completely. However, the water-soluble polythiophenes are unsuitable for open conductor track structures, i.e. those exposed to the atmosphere.

The object of the invention was to find a process for producing open electrically conductive structures on substrates which is simpler and faster to carry out than the known processes of structuring using copper conductor tracks, and gives stable conductor track structures under normal conditions.

Thus, the present invention provides such a process by printing, onto a substrate, the conductive structures using an ink-jet printer or X,Y plotter in the cartridge of which there is an aqueous dispersion of polyalkylenedioxythiophenes with a suitable polyanion as a counter anion.

The substrate used may be paper or plastic film.

The polyalkylenedioxythiophenes have been cationically charged and are composed of structural units of the formula (I)



(I)

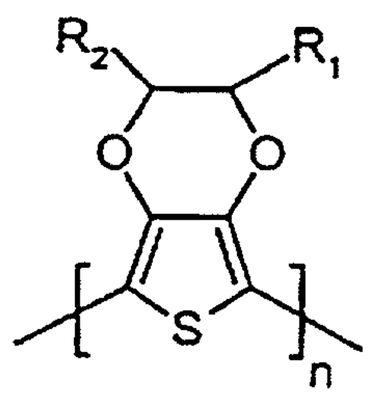
in which

A^1 and A^2, independently of one another, represent substituted or unsubstituted C_1-C_4-alkyl or together form a substituted or unsubstituted C_1-C_4-alkylene group, and

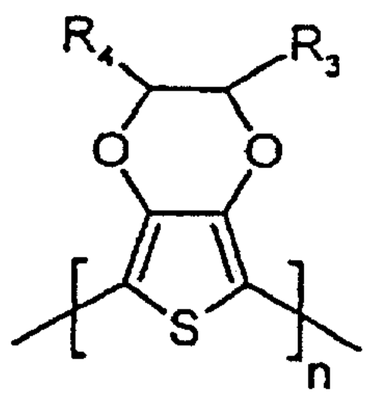
n represents an integer from 2 to 10,000, preferably from 5 to 5000,

in the presence of polyanions.

Preferred cationic polyalkylenedioxythiophenes are composed of structural units of the formula (Ia) or (Ib)



(Ia)



(Ib)

where

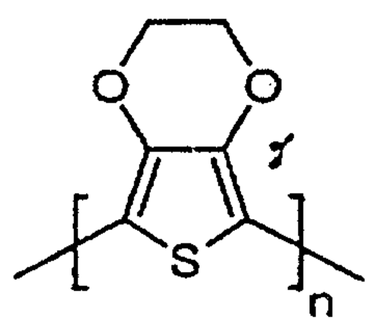
R_1 and R_2, independently of one another, represent hydrogen, substituted or unsubstituted C_1-C_{18}-alkyl, preferably C_1-C_{10}-alkyl, in particular C_1-C_6-alkyl, C_2-C_{12}-alkenyl, preferably C_2-C_8-alkenyl, C_3-C_7-cycloalkyl, preferably cyclopentyl or cyclohexyl, C_7-C_{15}-aralkyl, preferably phenyl-C_1-C_4-alkyl, C_6-C_{10}-aryl, preferably phenyl or naphthyl, C_1-C_{18}-alkyloxy, preferably

C_1-C_{10}-alkyloxy, such as methoxy, ethoxy, n-propoxy or isopropoxy, or C_2-C_{18}-alkyloxy esters, and

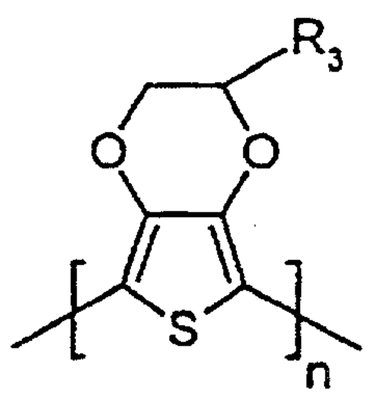
R_3 and R_4, independently of one another, represent hydrogen, but not both simultaneously, or at least singly sulphonate-substituted C_1-C_{18}-alkyl, preferably C_1-C_{10}-alkyl, in particular C_1-C_6-alkyl, C_2-C_{12}-alkenyl, preferably C_2-C_8-alkenyl, C_3-C_7-cycloalkyl, preferably cyclopentyl or cyclohexyl, C_7-C_{15}-aralkyl, preferably phenyl-C_1-C_4-alkyl, C_6-C_{10}-aryl, preferably phenyl or naphthyl, C_1-C_{18}-alkyloxy, preferably C_1-C_{10}-alkyloxy, such as methoxy, ethoxy, n-propoxy or isopropoxy, or C_2-C_{18}-alkyloxy esters, and

n represents a number from 2 to 10,000, preferably from 5 to 5000.

Particular preference is given to cationic or neutral polyalkylenedioxythiophenes of the formulae (Ia-1) and/or (Ib-1)



(Ia-1)



(Ib-1)

where

R_3 is as defined above, and

n represents an integer from 2 to 10,000, preferably from 5 to 5000.

The polyanions comprise anions of polymeric carboxylic acids, for example polyacrylic acids, polymethacrylic acids or polymaleic acids, and of polymeric sulphonic acids, such as polystyrenesulphonic acids and polyvinylsulphonic acids. These polycarboxylic and polysulphonic acids may also be copolymers of

vinylcarboxylic and vinylsulphonic acids with other polymerizable monomers, such as acrylates and styrene.

The gegenion particularly preferably comprises the anion of polystyrenesulphonic acid (PSA).

The molecular weight of the polyacids supplying the polyanions is preferably from 1000 to 2,000,000, particularly preferably from 2000 to 500,000. The polyacids or their alkali metal salts are available commercially, e.g. polystyrenesulphonic acids and polyacrylic acids, or else can be prepared by known processes (see, for example, Houben Weyl, Methoden der organischen Chemie [Methods in Organic Chemistry], Vol. E 20 Makromolekulare Stoffe, Part 2, (1987), pp. 1141 et seq.).

Instead of the free polyacids required for forming the dispersions of polyalkylenedioxythiophenes and polyanions, it is also possible to use mixtures of alkali metal salts of the polyacids and appropriate amounts of monoacids.

In the case of formula (Ib-1) the polyalkylenedioxythiophenes carry positive and negative charge in the structural unit.

The preparation of the polyalkylenedioxythiophenes is described, for example, in EP-A 0 440 957 (= US-A 5 300 575). The polyalkylenedioxythiophenes are prepared by oxidative polymerization. This gives them positive charges which are not represented in the formulae, since their number and position cannot be established beyond question.

An advantage of the novel process is that open, electrically conductive structures can be produced on printed circuit boards with quality comparable to that of the known copper conductor tracks, but in a small number of steps which are easy to carry out. All that is needed for production is an ink-jet printer with an appropriately prepared printer cartridge and a computer to control the printer. The desired conductor track structure can be designed on the computer screen and immediately printed out on a suitable substrate.

The water-dispersible polyalkylenedioxythiophene is not water-soluble and, even under normal conditions, forms a conductive structure which has long-term stability.

Figures and examples

The figures show:

Fig. 1 Bayer cross symbols printed on paper using poly-(3,4-ethylenedioxy-thiophene) (PEDT) and polystyrene sulphonate (PSS).

Fig. 2 Conductor track system printed onto paper using PEDT/PSS.

Fig. 3 Conductor track system printed onto polyethylene terephthalate (PET) film using PEDT/PSS.

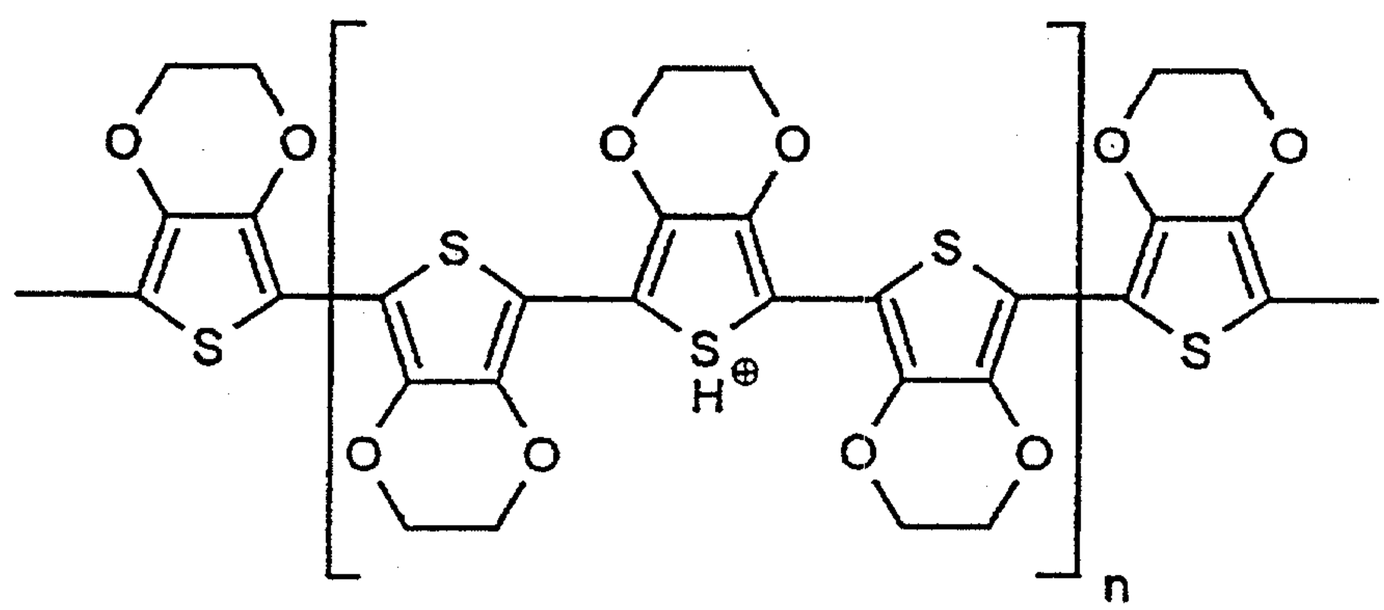
Example 1

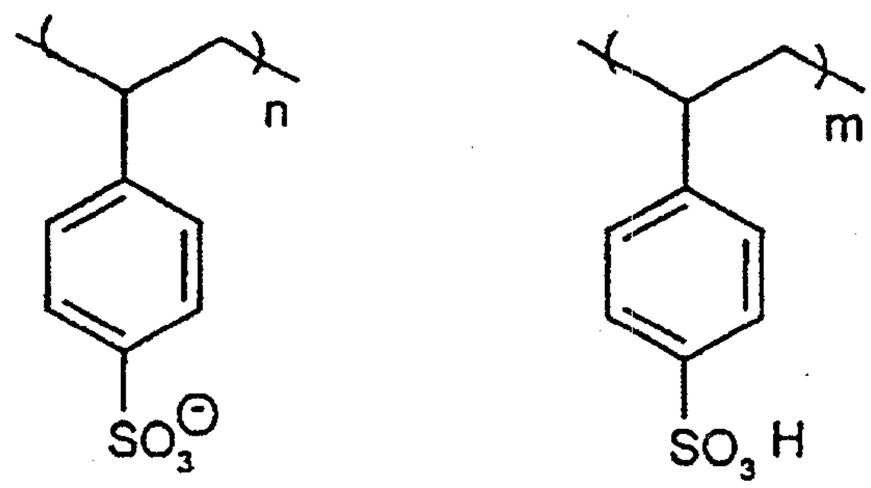
Preparation of the 3,4-polyalkylenedioxythiophene dispersion

20 g of free polystyrenesulphonic acid (Mn about 40,000), 21.4 g of potassium peroxodisulphate and 50 mg of iron(III) sulphate were stirred in 2000 ml of water. 8.0 g of 3,4-ethylenedioxythiophene were added, with stirring. The dispersion was stirred for 24 h at room temperature. 100 g of anion exchanger (commercially available product Lewatit MP 62 from Bayer AG) and 100 g of cation exchanger (commercially available product Lewatit S 100 from Bayer AG) were added, both in moistened form, followed by stirring for 8 hours.

The ion exchangers were removed by filtering through a polyacrylonitrile fabric of pore size 50 µm. This gave a ready-to-use dispersion of 3,4-polyalkylenedioxy-thiophenes (PEDT) with polystyrenesulphonate (PSS) as gegenanion (see II) with a solids content of about 1.2% by weight.

The dispersion could easily be filtered through a 0.45 µm filter and was used after filtration to prepare the colours for the ink-jet printer.





(II)

Example 2

The aqueous dispersion of the PEDT/PSS as in (II) from Example 1 was introduced into an empty ink-jet printer cartridge for an HP-Desk-Jet PLUS (Hewlett-Packard) ink-jet printer. The cartridge had been cut open and thoroughly cleaned and after the PEDT/PSS dispersion as in (II) had been introduced it was sealed again using a polyethylene hot-melt adhesive from Henkel. An ink-jet printer cartridge prepared in this way was inserted into the HP-Desk-Jet PLUS ink-jet printer and served as a reservoir for the printing liquid for applying the PEDT/PSS dispersion using the printer under computer control. The pattern to be printed was designed on the computer using a conventional software program. An image of three Bayer cross symbols placed under one another (Fig. 1) was selected. This image was printed onto paper using computer control. The result was a print on paper of the three Bayer cross symbols placed one underneath the other and composed of conductive PEDT/PSS, which had a blue intrinsic colour.

Example 3

The procedure followed was similar to that of Example 2, except that a polyethylene terephthalic (PET) film of 0.1 mm thickness was used instead of the paper and printed with the Bayer cross symbols.

Example 4

The procedure followed was similar to that of Example 2, except that the pattern was a section for a printed circuit board designed using EAGLE layout software (Fig. 2).

This conductor track pattern was printed onto paper using PEDT/PSS as in Example 3.

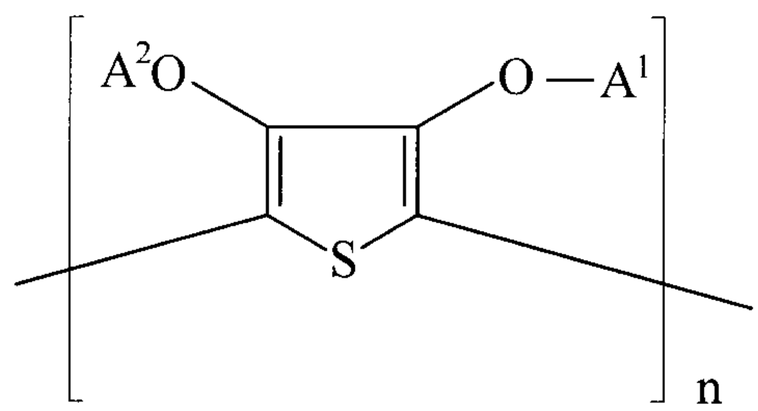
Example 5

In a manner similar to that of Example 4, the conductor track system of Fig. 3 was printed onto a PET film of 0.1 mm thickness. The electrical conductivity of the printed conductor tracks was demonstrated using a continuity tester.

CLAIMS:

1. A process for preparing an open electrically conductive structure on a substrate, which comprises printing the open electrically conductive structure onto the substrate using an ink-jet printer or X,Y plotter in the cartridge of which there is an aqueous dispersion of a polyalkylenedioxythiophene having a suitable polyanion as a counter anion.

2. The process according to claim 1, wherein the polyalkylenedioxythiophene is cationically charged and is composed of a structural unit of the formula (I):



(I)

in which:

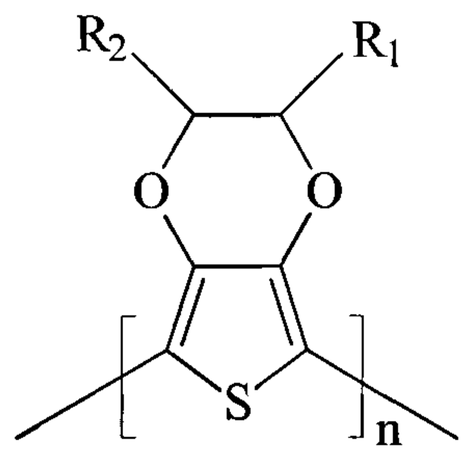
A^1 and A^2, independently of one another, represent a substituted or unsubstituted C_1-C_4-alkyl, or together form a substituted or unsubstituted C_1-C_4-alkylene group, and

n represents an integer from 2 to 10,000,

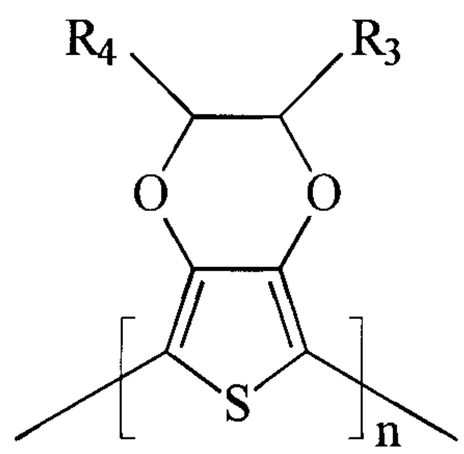
in the presence of the polyanion.

3. The process according to claim 2, wherein n represents an integer of from 5 to 5000.

4. The process according to claim 1, wherein the cationic polyalkylenedioxythiophene is composed of a structural unit of the formula (Ia) or (Ib):



(Ia)



(Ib)

where:

R_1 and R_2, independently of one another, represent hydrogen, substituted or unsubstituted C_1-C_{18}-alkyl, C_2-C_{12}-alkenyl, C_3-C_7-cycloalkyl, C_7-C_{15}-aralkyl, C_6-C_{10}-aryl, C_1-C_{18}-alkyloxy, or C_2-C_{18}-alkyloxy esters, and

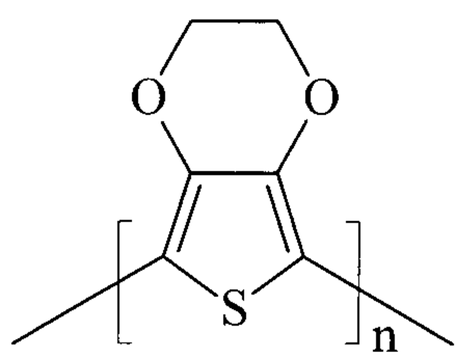
R_3 and R_4, independently of one another, represent hydrogen, or at least singly sulphonate-substiuted C_1-C_{18}-alkyl, C_2-C_{12}-alkenyl, C_3-C_7-cycloalkyl, C_7-C_{15}-aralkyl, C_6-C_{10}-aryl, C_1-C_{18}-alkyloxy, or C_2-C_{18}-alkyloxy ester, provided that R_3 and R_4 do not simultaneously represent hydrogen, and

n represents a number from 2 to 10,000.

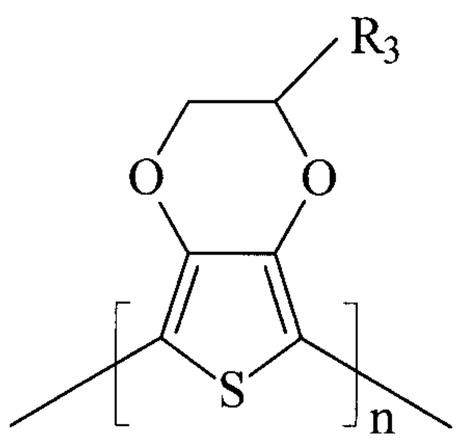
5. The process according to claim 4, wherein the structural unit has the formula (Ia) where R_1 and R_2, independently of one another, represent hydrogen, C_1-C_{10}-alkyl, C_2-C_8-alkenyl, cyclopentyl, cyclohexyl, phenyl-C_1-C_4-alkyl, phenyl, naphthyl, or C_1-C_{10}-alkyloxy; and n represents a number from 5 to 5000.

6. The process according to claim 4, wherein the structural unit has the formula (Ib) where R_3 and R_4, independently of one another, represent hydrogen or at least singly sulfonate-substituted C_1-C_{10}-alkyl, C_2-C_8-alkenyl, cyclopentyl, cyclohexyl, phenyl-C_1-C_4-alkyl, phenyl, naphthyl or C_1-C_{10}-alkoxy, provided that R_3 and R_4 do not simultaneously represent hydrogen; and n represents a number from 5 to 5000.

7. The process according to claim 1, wherein the cationic polyalkylenedioxythiophene is composed of at least one of structural units of the formulae (Ia-1) and (Ib-1)



(Ia-1)



(Ib-1) ;

where:

R_3 is hydrogen or at least singly sulfone-substituted C_1-C_{18}-alkyl, C_2-C_{12}-alkenyl, C_3-C_7-cycloalkyl, C_7-C_{15}-aralkyl, C_6-C_{10}-aryl, C_1-C_{18}-alkyloxy or C_2-C_{18}-alkyloxy ester, and

n represents an integer from 2 to 10,000,

and the polyanion comprises an anion of a polymeric carboxylic acid or a polymeric sulphonic acid.

8. The process according to claim 7, wherein the cationic polyalkylenedioxythiophene is composed of the structural unit of the formula (Ia-1).

9. The process according to claim 7, wherein the cationic polyalkylenedioxythiophene is composed of the structural unit of the formula (Ib-1).

10. The process according to any one of claims 7 to 9, wherein n is an integer from 5 to 5000.

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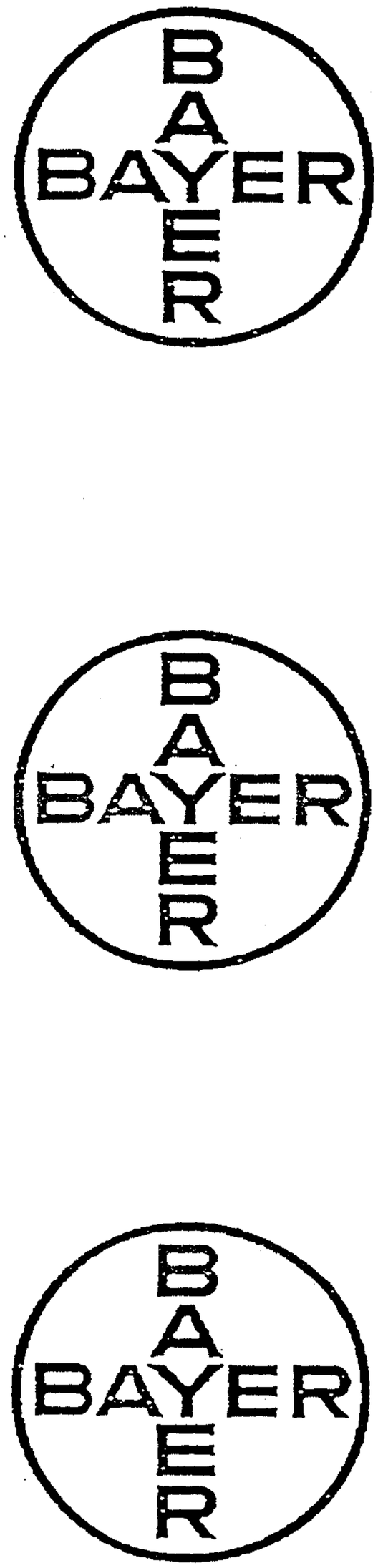

Fig. 1

Le A 33 106-Foreign Countries

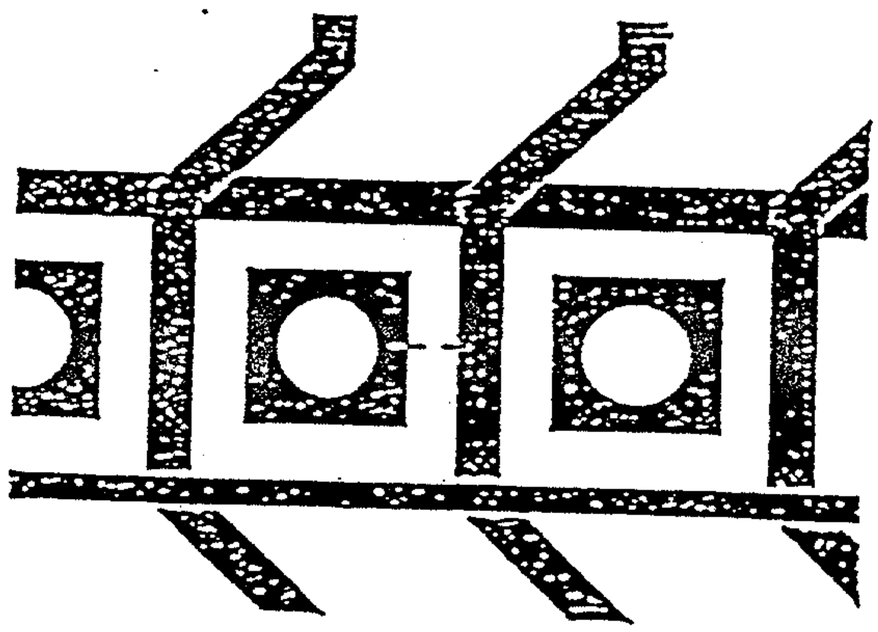

Fig. 2

Le A 33 106-Foreign Countries

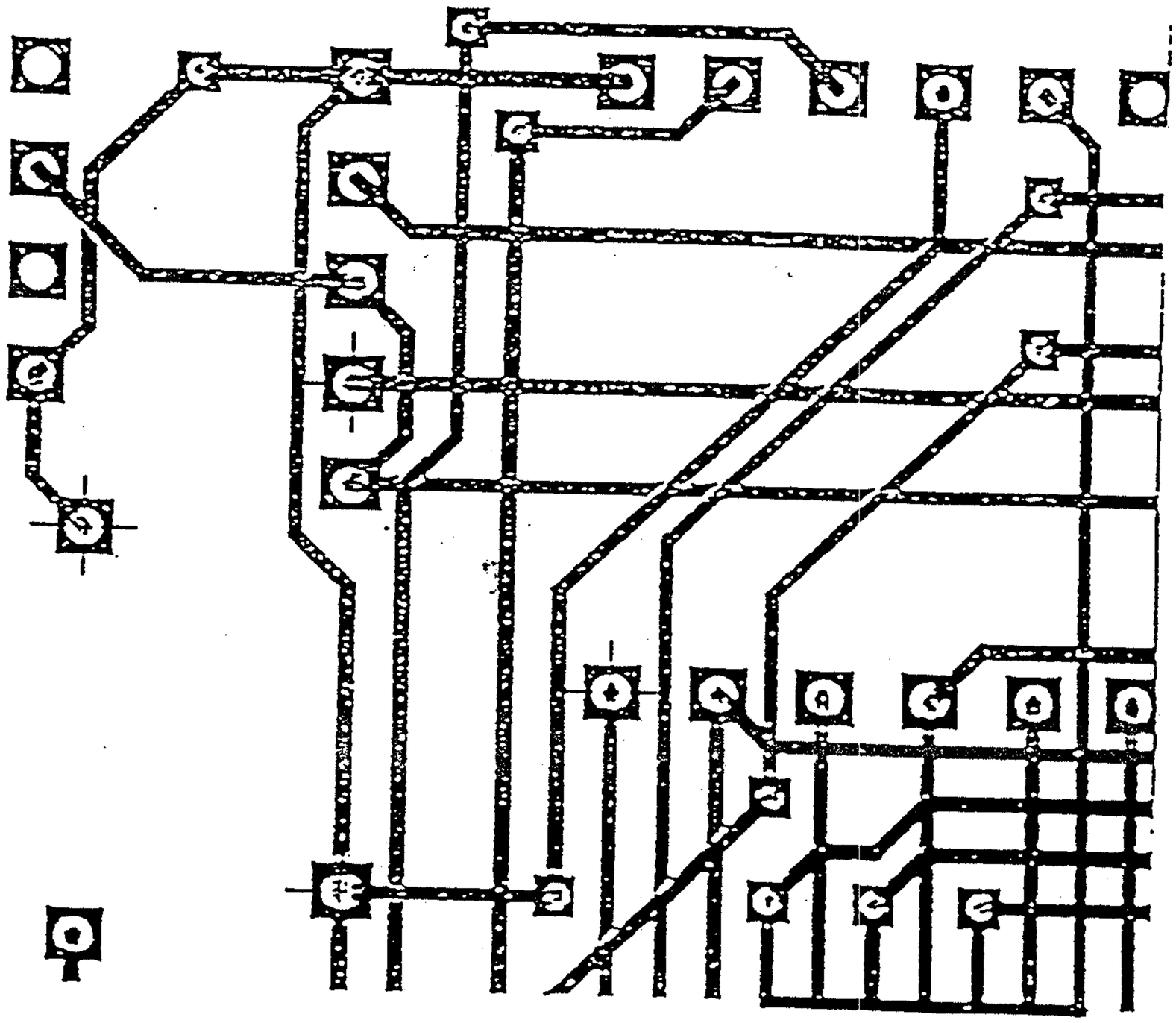
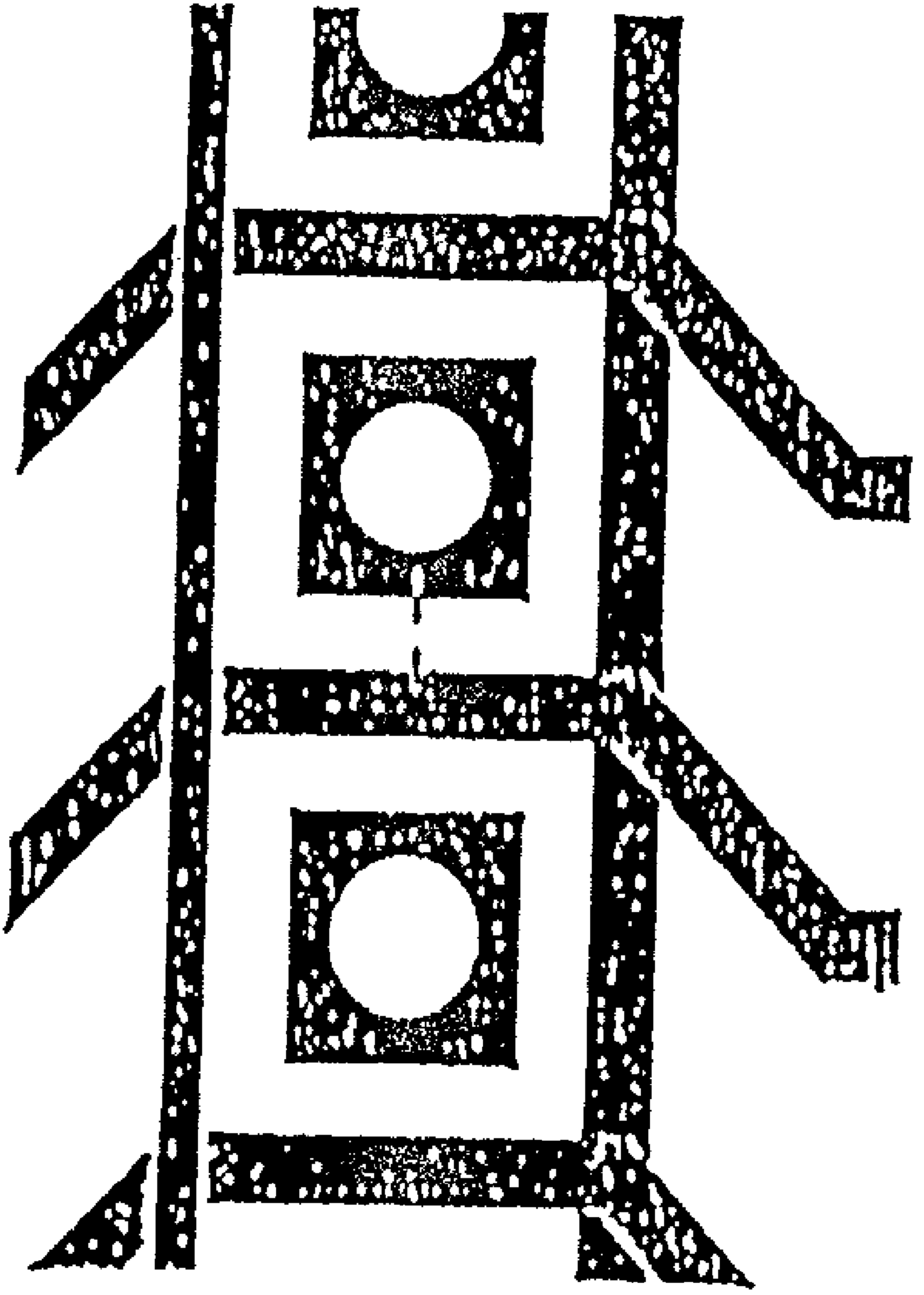
Fig. 3