(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 January 2002 (03.01.2002)

PCT

(10) International Publication Number
WO 02/00966 A1

(51) International Patent Classification[7]: C25D 1/10

(21) International Application Number: PCT/NL01/00479

(22) International Filing Date: 27 June 2001 (27.06.2001)

(25) Filing Language: Dutch

(26) Publication Language: English

(30) Priority Data:
1015535 27 June 2000 (27.06.2000) NL

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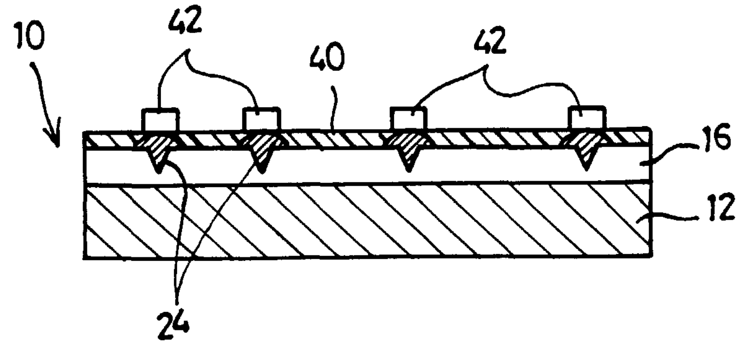
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ELECTROFORMING DIE, METHOD OF MANUFACTURING THE SAME, APPLICATION THEREOF AND ELECTROFORMED PRODUCTS



(57) Abstract: The invention relates to an electroforming die (10) for the electroforming of products, which die comprises a structure of interconnected, electrically conductive metal die tracks, the structure comprising a random, disordered network (32) of electrically conductive die tracks. A network of this type can be obtained, for example, by the preferential electroplating of (micro)cracks (18) in an electroformed metal surface (20), such as of a chromium layer (16). A method for the production of the die, and its application, as well as products (42) electroformed therewith, such as printing screens and battery electrodes, are also described.

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ELECTROFORMING DIE, METHOD OF MANUFACTURING THE SAME, APPLICATION THEREOF AND ELECTROFORMED PRODUCTS

The present application relates firstly to an electroforming die for the electroforming of metal products, which electroforming die comprises a structure of interconnected, electrically conductive die tracks.

An electroforming die of this type is generally known in the art and is used for the electroforming of metal products in electrodeposition baths, in which metal is deposited on the structure of electrically conductive die tracks, which die tracks are connected to a suitable current source. An example of products which are electroformed in this way with openings separated by product dykes, the structure of the product dykes which are formed corresponding to the structure of the die tracks of the electroforming die, is printing screens, both flat and cylindrical, which are used for the screen-printing of substrates, such as textiles and paper. Another example is an electrode for use in batteries, in which an electrolyte paste is held in and on the product. In the known electroforming die, the structure of the die tracks has a regular pattern on account of the way in which it is produced, including in general a photoresist layer which has been applied to an electrically conductive substrate being exposed and developed in pattern form and, depending on the type of photoresist - negative or positive - the exposed or unexposed parts being removed and the photoresist pattern which remains being stoved, after which the structure of electrically conductive die tracks, in this case die dykes which project above the main surface of the electrically conductive substrate, is deposited by galvanization to the desired thickness on the exposed, electrically conductive substrate parts between the islands of photoresist. Consequently, a product which is electroformed using a die produced in this way also has a regular pattern of openings separated by product dykes.

One of the problems which may be caused by a printing screen with a regular pattern of printing openings separated by product dykes is the Moiré effect. This effect may arise when two or more regular patterns are superimposed.

When using the known printing screen, a photosensitive resist is applied thereto and is then exposed, developed and cured by a grid film which comprises a copy of the image to be printed in grid form, so that a regular pattern of openings in the region of the image to be printed is also present in the photoresist layer. Therefore, during printing there are two regular patterns, one comprising the screen-printing openings and one comprising the openings in the photoresist layer, resulting in the Moiré effect, so that the quality of the printed image generally deteriorates. In addition, the regular pattern of the screen-printing openings, in combination with a regular pattern of the substrate to be printed, for example in the case of textiles, may give rise to the Moiré effect, although the effect in the latter case is less pronounced than in the former case.

The broad object of the present invention is to reduce or even eliminate the occurrence of this effect.

In the electroforming die of the abovementioned type according to the invention, the structure comprises a random, disordered network of electrically conductive die tracks.

The invention is based on the insight that the occurrence of the abovementioned Moiré effect can be prevented by changing at least one of the two interacting patterns, either that of the screen-printing openings or that of the openings in the photoresist layer (or in the substrate), into a disordered collection of openings. Since the pattern in the photoresist layer corresponds to the grid film of a digitized image, it is difficult to randomize this pattern. However, it is possible to random, disordered (randomize) the pattern of openings in the printing screen by adapting the electroforming die used for the production of these screens, which according to the invention comprises a random, disordered network of die tracks. If a printing screen is produced in the customary way using the electroforming die with such a random, disordered network of die tracks according to the invention, the printing screen will comprise a corresponding random, disordered network of product dykes, which product dykes delimit the continuous printing openings. When printing a substrate using the printing screen which has been produced using the electroforming die according to the invention and likewise has such a random, disordered network, the Moiré effect consequently cannot occur, since there are no longer regular patterns which overlap one another. In this way, the printing quality is improved.

In this context, it should be noted that where the present text uses the term "random, disordered network", this is intended to mean an irregular grid which generally does not repeat itself but of which some parameters, such as its number of lines and thickness, can be controlled, but the direction cannot be controlled.

It will be understood that the random, disordered network of die tracks may comprise some regular elements, provided that the die overall can be considered to be a random, disordered network. By way of example, the network may comprise a rough pattern of lines of (reinforcing) die tracks which in each case delimit partial areas with a disordered network of die tracks.

The products produced using the electroforming die according to the invention can also be used for other purposes, such as electrodes in batteries, in which case electrolyte (paste) is situated in the openings and on the product dykes of the electrode, which therefore also functions as a carrier for electrolyte. A further example of an electroformed product of this type is a die for the perforation of plastic sheets, in which the sheet is applied to one side of the die and, as a result of vacuum being applied to the other side of the die, is sucked into the openings in the die until holes are formed in the sheet at these locations.

The die tracks may comprise dykes which project above the surface, but may also be recesses in the surface or a mixture of the two.

The electroforming die according to the invention preferably comprises a layered structure, comprising an electrically conductive base layer, advantageously made from a metal of good conductivity, such as solid copper, a top layer which comprises electrically conductive metal and has a random, disordered network of small cracks at least in the surface which is remote from the base layer, the random, disordered network of electrically conductive die dykes being present at least in the random, disordered network of cracks. It has been found that (micro)cracks in a surface of a first metal can be preferentially filled up with another metal under standard electroforming conditions. Microcracks of this type are formed, for example, in electroplated chromium, varying in number from fewer than 4 to approximately 3200 per linear centimetre, depending, inter alia, on bath composition, current density and temperature. In general, the number of microcracks in hard chromium is approximately 1200 per linear centimetre. Incidentally, it should be noted at this point that the phenomenon of microcracking in chromium of this type and the factors which influence the number of cracks have long been known (cf. for example "Microcracks in hard chromium electrodeposits" by A.R. Jones and "Dekorative Chrom-Nickel-Überzüge", by W. Blum). Furthermore, it is known to determine the number of cracks/pores in a chromium layer by selective deposition, under specific conditions, of copper in these cracks and pores and measuring the weight of the deposited copper or the amount of current used for the deposition. However, the use of these phenomena to obtain an arbitrary network of electroformed metal has never previously been taken into consideration. It is assumed that microcracks are also formed in Cr alloys, and other metals or metal alloys with a high internal stress. Another possibility for obtaining a virtually random, disordered network of scratches is to apply a suitably hard brush to a smooth metal surface.

In this context, it should be pointed out that if a chromium layer is deposited by known methods for the production of an electroforming die, it is afterwards ground in order to activate the chromium by removal of the low-conductivity chromium oxide skin which is present, with the result that the possibility of preferential metal deposition as used in the production of the electroforming die according to the present invention is lost. Therefore, in the electroforming die according to the invention, it is preferable to use non-activated chromium as material for the top layer of the layered structure.

This means that the expression "electrically conductive" in the present application is a relative term; the material which surrounds the electrically conductive die tracks may also be electrically conductive, but should be considered a non-conductive material compared to the electrically conductive die tracks under the electroforming conditions employed.

A basic embodiment of the electroforming die therefore comprises an electrically conductive base layer, advantageously made from a metal of good conductivity, such as copper, with a top layer, of which the surface is relatively non-conductive, with a random, disordered network of electrically conductive die tracks in the form of die recesses in this layer. This basic embodiment is suitable for making flat products, provided it is possible to remove these products from the die recesses, for example by peeling.

The thickness of the top layer is advantageously greater than the depth of the (micro)cracks, so as to limit the risk of a product which has been produced using the electroforming die "sticking" to the metal of the base layer, i.e. being impossible to remove.

The electrically conductive material which forms the die dykes in the cracks in the top layer in the electroforming die of layered structure advantageously consists of nickel. If the nickel of the die dykes is passivated in a way which is known per se in the prior art, for example with the aid of potassium permanganate or potassium bichromate, and those parts of the top layer which are exposed between the die dykes of the network are covered with photoresist or other electrically insulating material, the thickness of which is less than or equal to the height of the die dykes above the upper surface of the top layer, the result is a die which is suitable for the production of flat or cylindrical products, depending on the form of the base layer.

The present invention also relates to a method of manufacturing an electroforming die, which method comprises the steps of:

(a) creating an electrically conductive base layer;

(b) providing an electrically conductive top layer with a random, disordered network of cracks in at least the upper surface of the top layer; and, if desired,

(c) the preferential deposition of an electrically conductive material in the cracks in the top layer, in order to form a random, disordered network of electrically conductive die dykes.

As has already been discussed extensively above, a top layer of an electrically conductive metal or metal alloy, preferably a chromium layer, is electrodeposited on a solid conductor, such as a copper layer, which top layer is then not activated. In that case, the cracks form electrically conductive die recesses, as explained above for the basic embodiment. If desired, an electrically conductive material, advantageously nickel, is then deposited in the microcracks which have formed during the deposition of the top layer. This is because nickel is a better conductor than the surface of the top layer of chromium. The method may comprise an additional step (d) of depositing an insulating material in the recesses between the electrically conductive die dykes prior to use, and the additional step (e) of passivating the nickel surface.

The invention also relates to the application of an electroforming die according to the invention in the electroforming the microcracks which have formed during the deposition of the top layer. This is because nickel is a better conductor than the surface of the top layer of chromium. The method may comprise an additional step (d) of depositing an insulating material in the recesses between the electrically conductive die dykes prior to use, and the additional step (e) of passivating the nickel surface.

The invention also relates to the application of an electroforming die according to the invention in the electroforming of products, as defined in claim 13.

The invention also relates to an electroformed product obtainable using an electroforming die according to the invention, which product is characterized by a random, disordered network of product dykes which are separated by spaces, in particular a printing screen as defined in claim 15 and an electrode for use in a battery as defined in claim 14. A (rotary) printing screen can be produced, for example, by allowing a thin skeleton to grow on the die according to the invention, and effecting preferential growth on this skeleton after it has been removed from the die, as described, for example, in EP-A-0 038 104, in the name of the applicant, or other methods which have been patented by the applicant.

The present invention is explained below with reference to the appended drawing, in which:

Figure 1 diagrammatically depicts an embodiment of an electroforming die according to the invention;

Figure 2 shows an example of a random, disordered network;

Figure 3 illustrates the application of the electroforming die shown in Fig. 1;

Figures 4 - 10 show photographs of various electroformed products according to the invention; and

Fig. 11 shows a basic embodiment of an electroforming die according to the invention.

Fig. 1 shows part of an electroforming die in section, in which the electroforming die is denoted overall by reference numeral 10. For the sake of simplicity, the figure shows a flat die 10, but it will be understood that a cylindrical die can also be produced using the same principles and may have the same structure. The electroforming die 10 illustrated comprises a base layer 12 of copper. An electroplated top layer 16 of chromium is present on its upper surface 14, which top layer, on account of the electroplating

This bath is used under conditions of a current density of 43 A/dm^2 and T = 60°C

Then, using a standard bath (for example a Watts bath) of nickel (total Ni^{2+} = 84 - 92 g/l; $NiCl_2$ = 14.5 - 15.5 g/l; H_3BO_3 = ± 40 g/l; meta(brightener) = 10 g/l and under standard conditions of a current density of 5 - 50 A/dm^2, T = 70°C and pH = 4.1, nickel was then preferentially deposited in the microcracks 18 in the non-activated chromium layer 16. This nickel was allowed to grow on until the upper edge 22 of the nickel die dykes 24 projects above the upper surface 20 of the chromium layer 16. In the situation illustrated, there has been some growth over this upper surface 20.

As can be seen from Fig. 2, the microcracks 18 form an irregular network 30. The nickel die dykes 24 will form a corresponding network. In other words, Fig. 2 likewise presents a network 32 of the die dykes 24. A regular sub-pattern of parallel "recesses" (corresponding to reinforcement dykes 26 for the die) is applied by machining the chromium layer 16 (for example by knurling). However, overall the networks 30 and 32 are irregular and disordered.

Prior to use, the die dykes 24 will usually be passivated with the aid, for example, of potassium bichromate, and the spaces 28 between the die dykes will be filled with photoresist 40 in the usual way (cf. also Fig. 3).

Fig. 3 illustrates the various steps of an embodiment of a method according to the invention for producing an electroforming die according to the invention, in which parts which correspond to components shown in Figs 1 and 2 are denoted by the same reference numerals.

Fig. 3 shows the same die as Fig. 1, with a solid copper layer 12, on which, after polishing, a chromium layer 16 in which there is a network 30 of microcracks 18 which extend a certain depth into the upper surface 20 is deposited. After any degassing which may be required, nickel is preferentially deposited in the microcracks 18, likewise by electrodeposition, which nickel forms dykes 24 corresponding to the network 30 of the microcracks 18. A thick layer of insulating material 40 is then applied to the entire surface of the chromium interlayer 16 and the nickel dykes 24, and this insulating material is then ground down as far as the upper surface of the dykes 24 (Fig. 3b).

The electroforming die produced in this way can be used for electroforming numerous products, as shown in Fig. 4, in which, by way of example, nickel is deposited from an electrodeposition bath on the die 10, more particularly on the nickel die dykes 24, as a thin skeleton 42, which is then removed from the die, followed by further growth on this skeleton in a suitable bath. The skeleton 42 will comprise the same random, disordered network of product dykes as the network 30 of the original microcracks 18.

Experiments have demonstrated that under the said conditions nickel can be preferentially deposited in the cracks of a 40 µm thick Cr layer which was formed on a base layer of copper, with the nickel product being readily removable.

Furthermore, it has been found that nickel is also preferentially deposited in scratches which have been formed in a Cr layer using a hard brush. By contrast, nickel was deposited over the entire surface of a scratched, oxidized copper roller.

Further results have shown that, under the same bath conditions, the thickness of the Cr layer has no effect on the mesh value of the electroformed product.

Figs. 4 - 10 show photographs taken using a scanning electron microscope (SEM) of products which have been electroformed using various electroforming dies according to the invention, Fig. a showing the bath side of a product which has been in contact with the electrolyte, while Fig. b shows the die side.

Fig. 11 shows a basic embodiment of an electroforming die according to the invention, which in principle is identical to the embodiment shown in Fig. 1, except that the electrically conductive die dykes 24 are absent, and instead the cracks 18 function as die recesses 60, on which an electroformed product can be made to grow. These die recesses 60 are better conductors than the surface of the top layer 20.

CLAIMS

1. Electroforming die for the electroforming of metal products, which electroforming die comprises a structure of interconnected, electrically conductive metal die tracks, characterized in that the structure comprises a random, disordered network (32) of electrically conductive die tracks.

2. Electroforming die according to claim 1, characterized in that the die tracks comprise die recesses (60).

3. Electroforming die according to claim 2, characterized in that the die (10) has a layered structure, comprising an electrically conductive metal base layer (12) with a top layer (16), of which the surface (20) is relatively non-conductive, with a random, disordered network (30) of cracks (18), which are electrically conductive die recesses (60), at least in the surface (20) which is remote from the base layer (12).

4. Electroforming die according to claim 1, characterized in that the die tracks comprise die dykes (24).

5. Electroforming die according to claim 4, characterized in that the die (10) has a layered structure, comprising an electrically conductive metal base layer (12), a top layer (16) with a random, disordered network (30) of cracks (18) at least in the surface (20) which is remote from the base layer (12), the random, disordered network (32) of electrically conductive die dykes (24) at least filling up the random, disordered network (30) of cracks (18).

6. Electroforming die according to one of the preceding claims, characterized in that the base layer (12) consists of solid copper.

7. Electroforming die according to one of the preceding claims, characterized in that the top layer (16) consists of chromium.

8. Electroforming die according to one of the preceding claims 4-7, characterized in that the random, disordered network (32) of die dykes (24) consists of nickel.

9. Electroforming die according to one of the preceding claims 4-8, characterized in that the spaces (28) between the electrically conductive die dykes (24) are filled up with an insulating material (40).

10. Electroforming die according to one of the preceding claims, characterized in that the random, disordered network (32) comprises a sub-pattern of regular pattern elements (26).

11. Electroforming die according to one of the preceding claims 4-9, characterized in that the random, disordered network (32) of electrically conductive dykes (24) consists of passivated nickel.

12. Method of manufacturing an electroforming die (10), which method comprises the following steps:

(a) creating an electrically conductive base layer (12);

(b) providing an electrically conductive top layer (16) with a random, disordered network (30) of cracks (18) in at least the upper surface (20) of the top layer (16).

13. Method according to claim 12, characterized by

(c) if desired, the preferential deposition of an electrically conductive material in the cracks (18) in the top layer (16), in order to form a random, disordered network (32) of electrically conductive die dykes (24).

14. Method according to claim 13, characterized in that the method comprises the additional step (d) of depositing an insulating material (40) in the spaces (28) between the electrically conductive dykes (24).

15. Method according to claim 13 or 14, characterized in that the electrically conductive material is nickel, and the method comprises the additional step (e) of passivating the nickel surface.

16. Method according to one of the preceding claims 12-15, characterized in that step (b) comprises the electroplating of a chromium layer (16).

17. Use of an electroforming die (10) according to one of claims

1-11 in the electroforming of products.

18. Electroformed product, obtainable using an electroforming die (10) according to one of claims 1-11, characterized by a random, disordered network of product dykes which are separated by spaces.

19. Electroformed printing screen, in particular rotary printing screen, for use in the screen-printing of substrates, obtainable using an electroforming die (10) according to one of claims 1-11, characterized by a random, disordered network of product dykes which are separated by openings.

20. Electroformed electrode, in particular for use in a battery, obtainable using an electroforming die (10) according to one of claims 1-11, characterized by a random, disordered network of product dykes which are separated by openings.

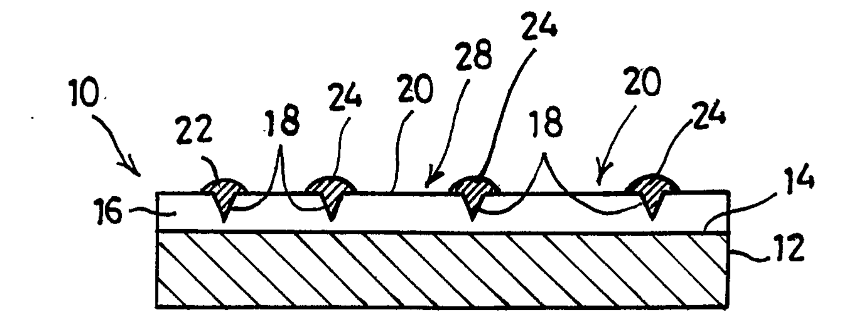

Fig: 1.

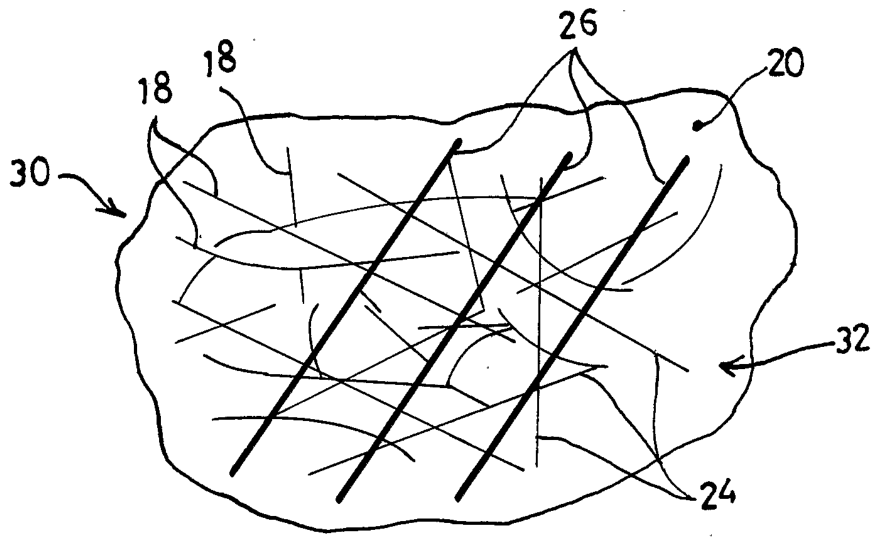

Fig: 2.

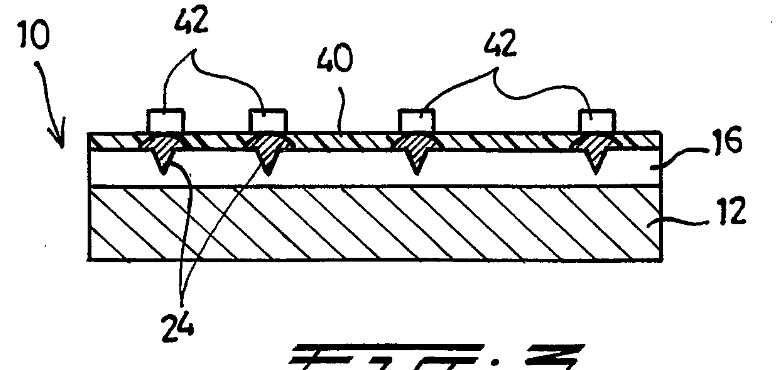

Fig: 3.

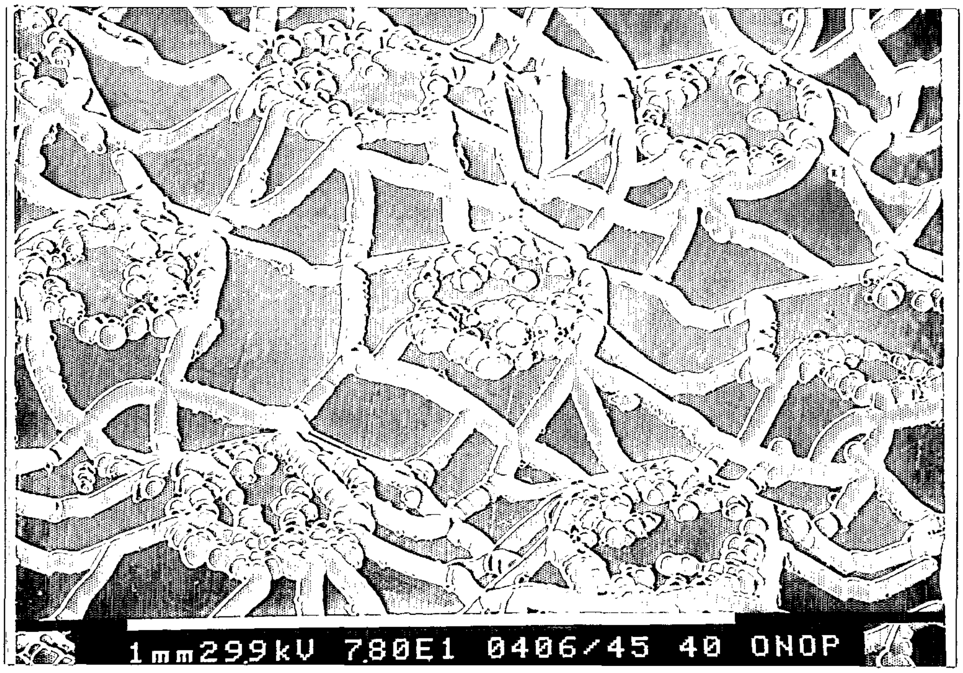

FIG 4A

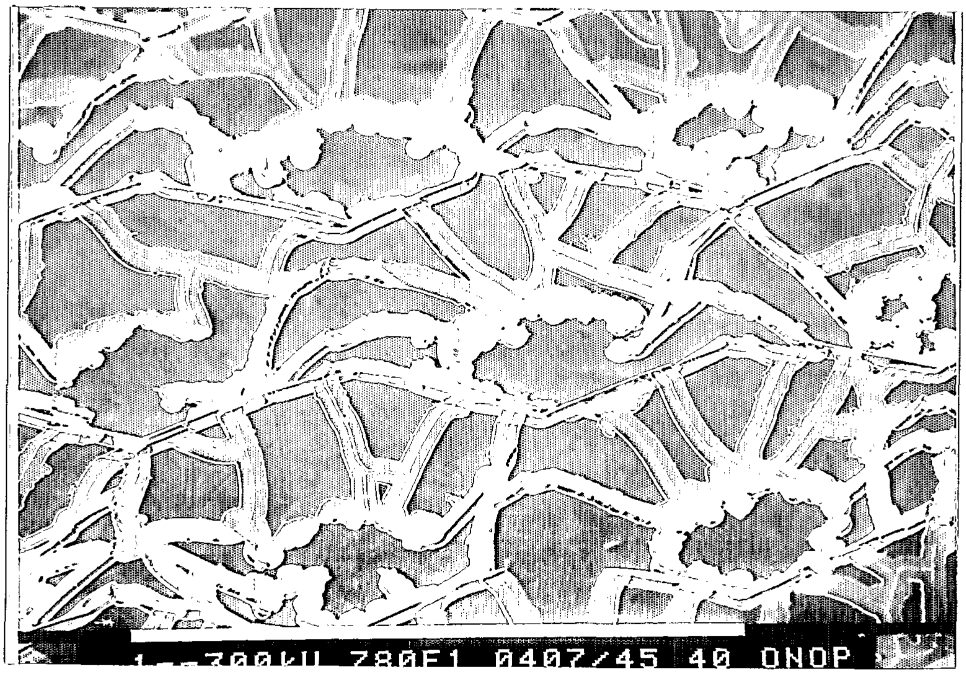

FIG 4B

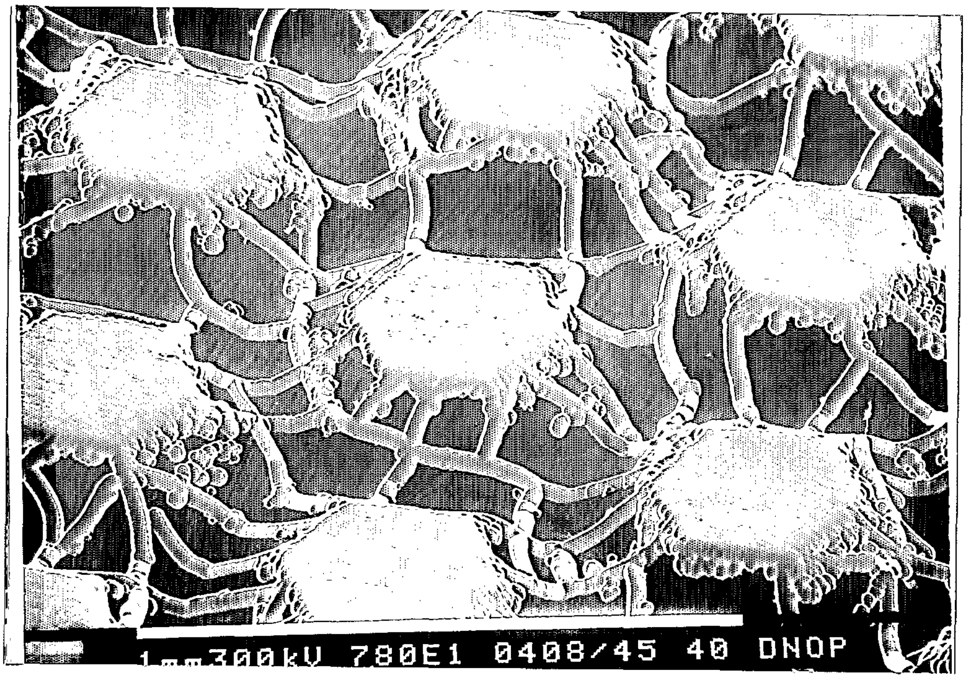
1mm300kV 780E1 0408/45 40 DNOP

FIG 5A

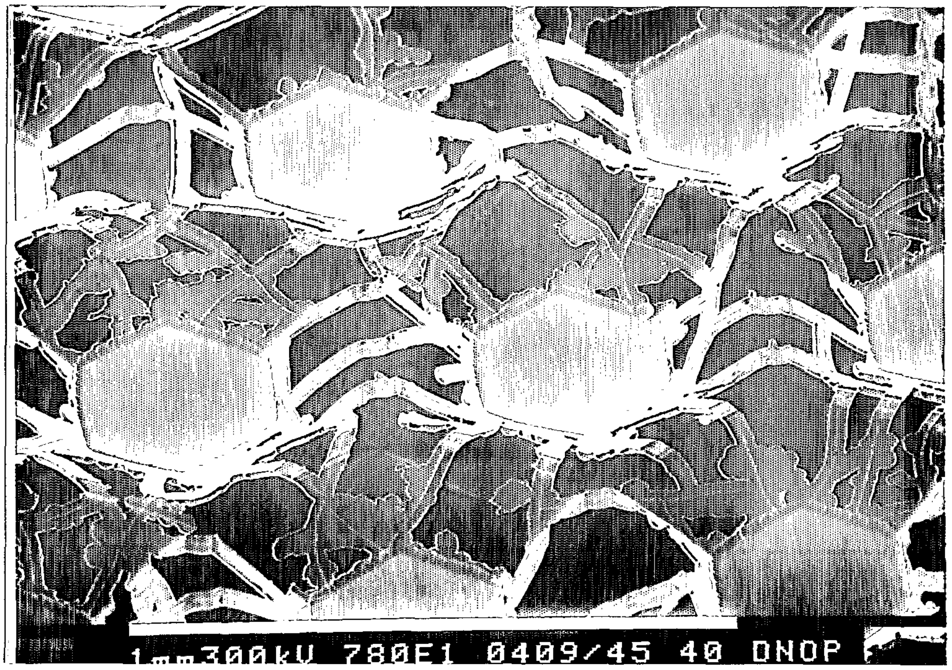
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FIG 5B

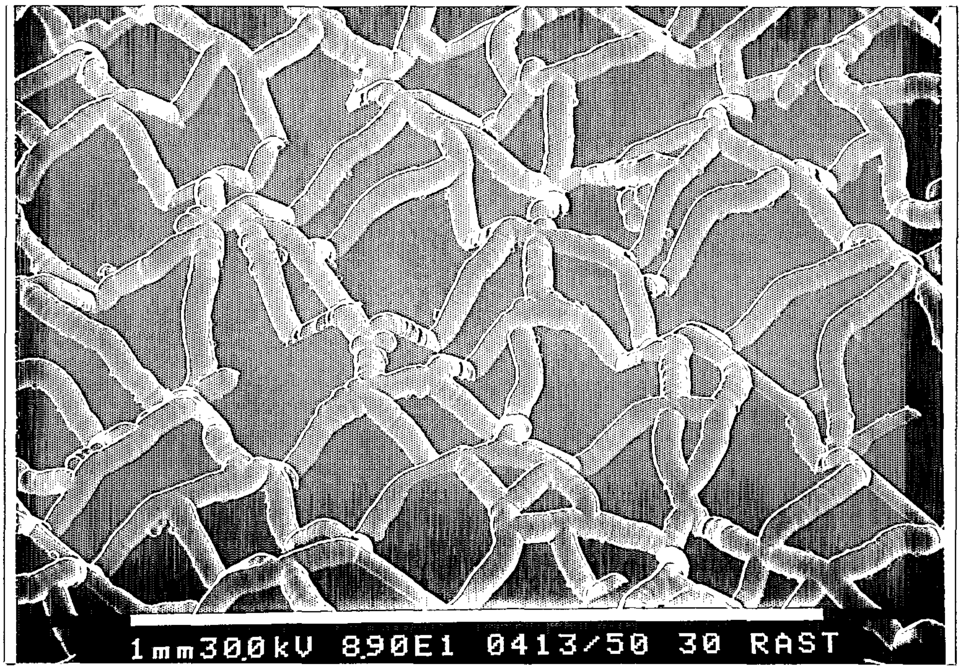
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FIG 6A

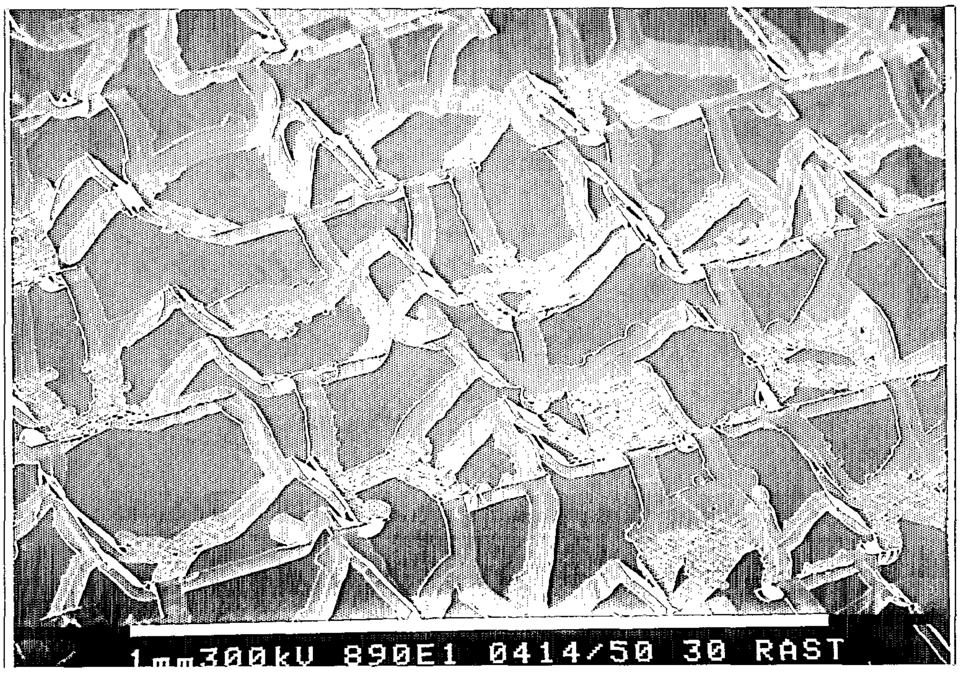
1mm300kV 890E1 0414/50 30 RAST

FIG 6B

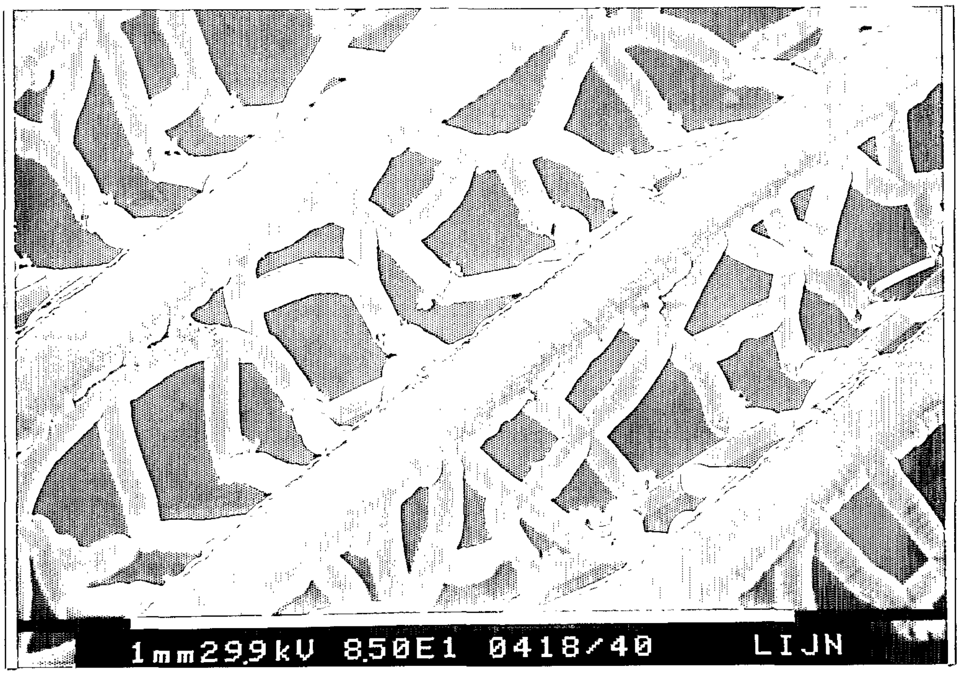

FIG 8A

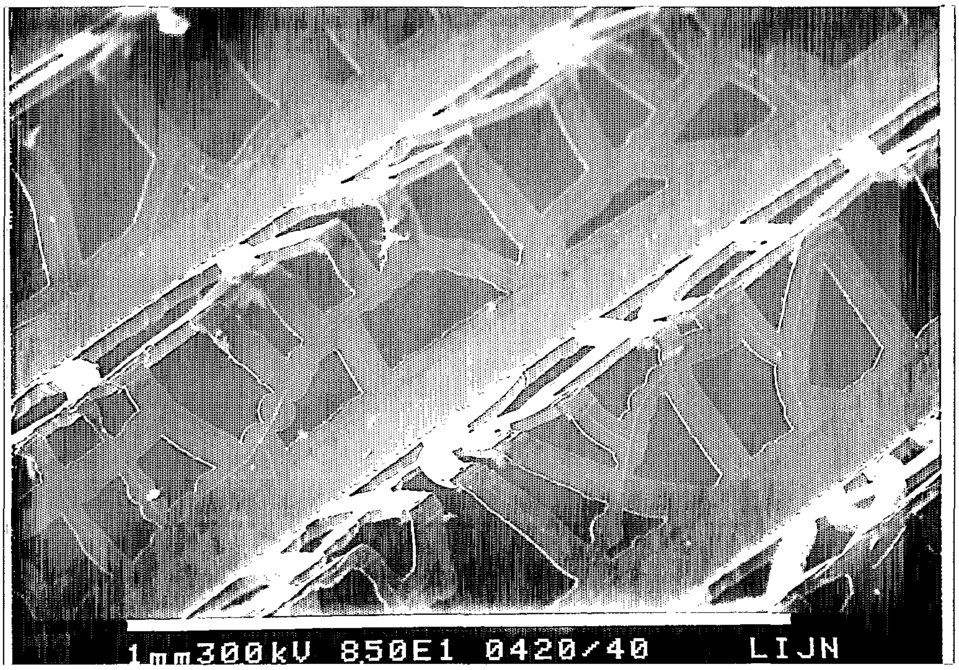

FIG 8B

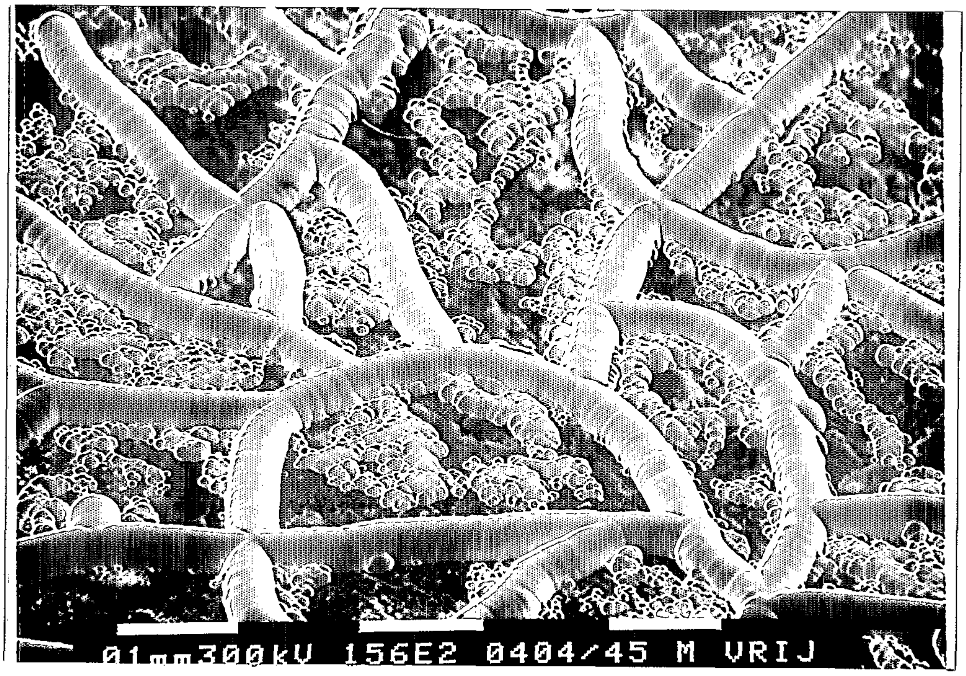
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FIG 9A

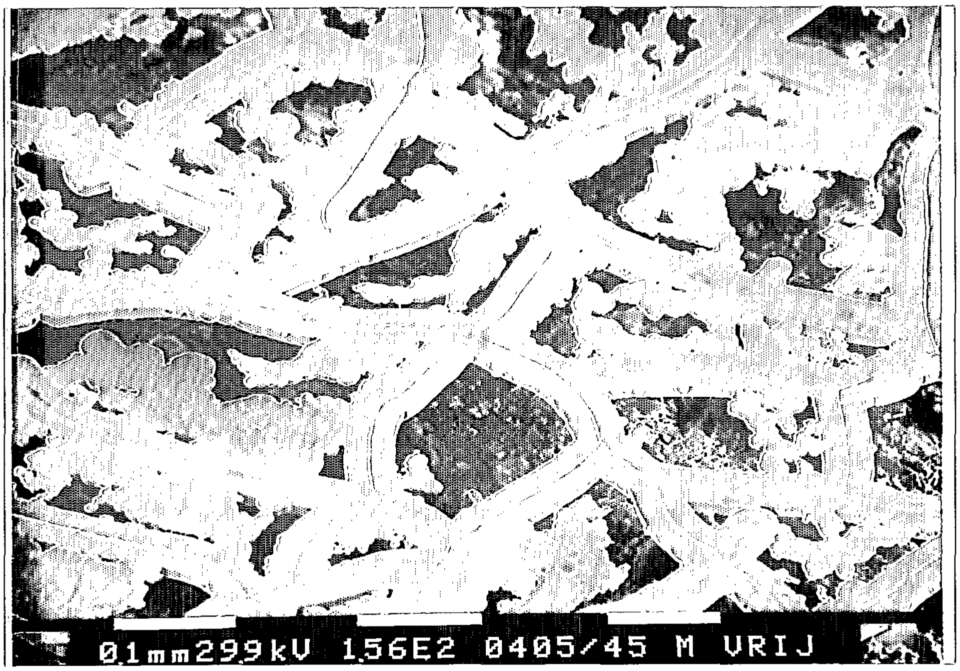
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FIG 9B

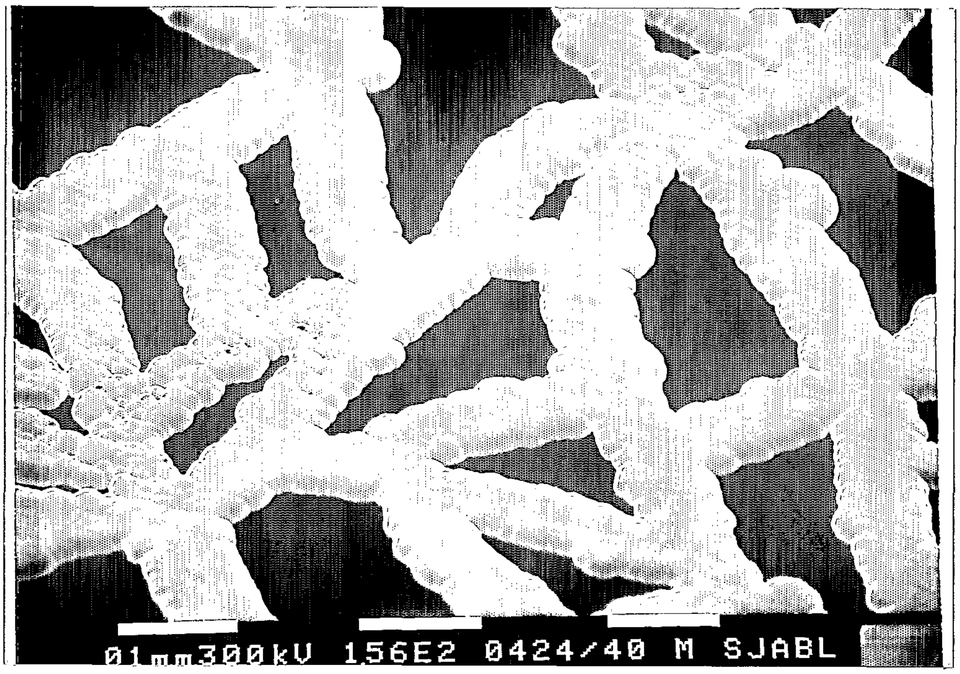

FIG 10A

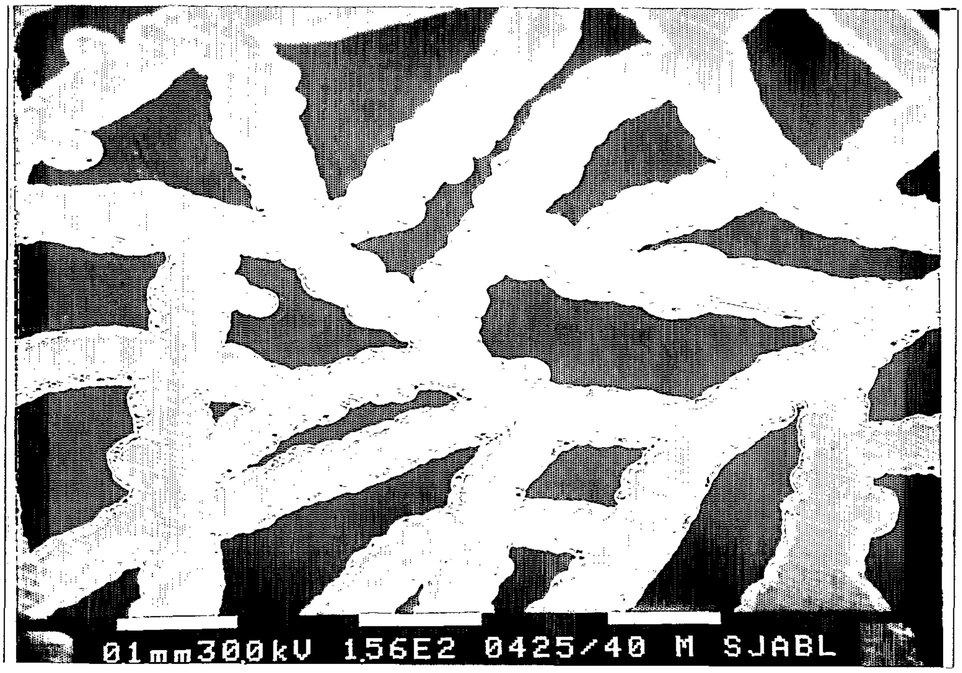

FIG 10B

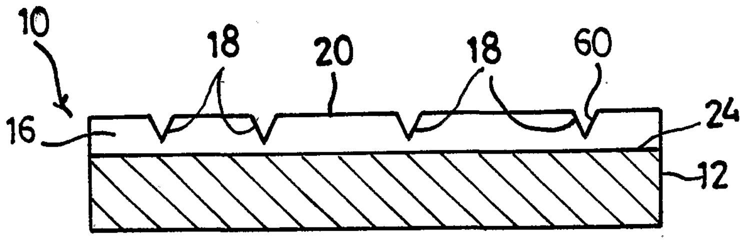

Fig: 11.

INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/NL 01/00479

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C25D1/10

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)
IPC 7 C25D

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 practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 891 514 A (KLEMM MARTIN) 24 June 1975 (1975-06-24) -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
8 October 2001	15/10/2001

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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