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(52) **U.S. Cl.** ..... **205/296**(75) **Inventor: Akiko Sugimoto, Saitama (JP)**

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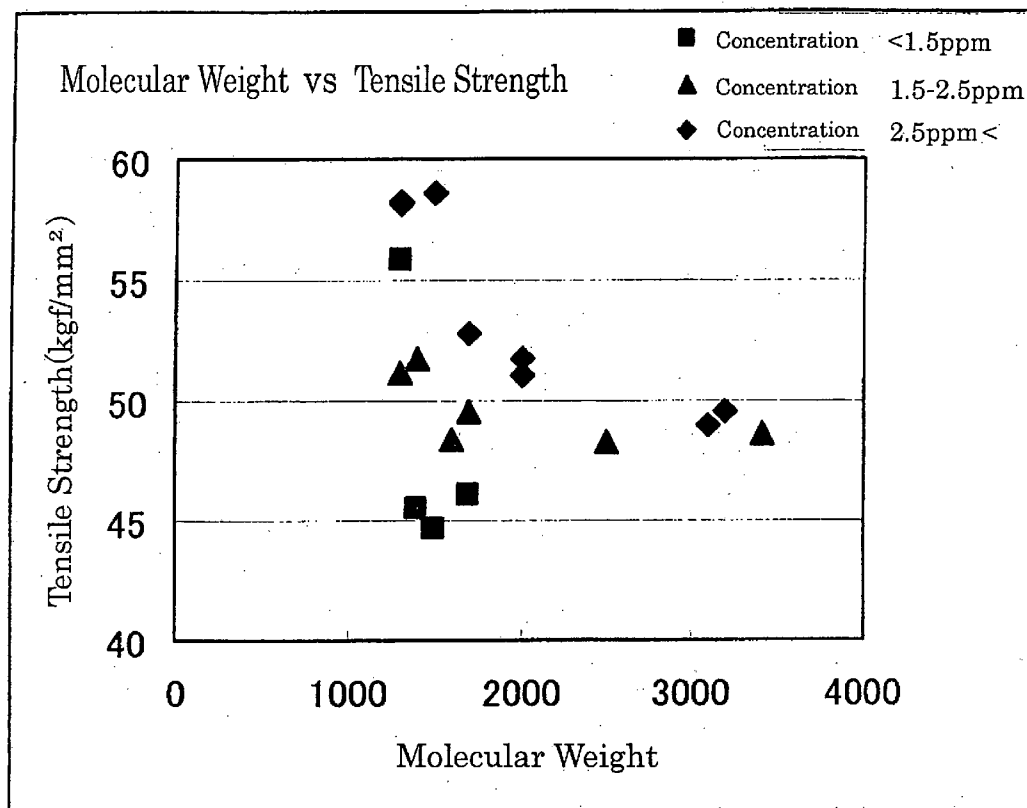
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(57) **ABSTRACT**

This invention is for providing a copper electrolyte solution producing an electrolytic copper foil capable of providing a foil in which the shape and size of mountains of the rough surface of the deposited foil are uniform and which has low roughness, substantially without decrease of the yield of deposited foil by controlling the molecular weight and the concentration of protein, etc. and a method of producing an electrolytic copper foil using the same.

In this copper electrolyte solution for producing an electrolytic copper foil, protein in the copper electrolyte solution preferably has a number average molecular weight  $M_n$  of 1000 to 2300 and the copper electrolyte solution preferably has a protein concentration of 2 to 4.5 ppm. The electrolyte solution preferably has  $\text{Cu}^{2+}$  concentration of 60 to 100 g/L. In addition, the electrolyte solution preferably has a free  $\text{SO}_4^{2-}$  concentration of 60 to 250 g/L. Also the electrolyte solution preferably has  $\text{Cl}^-$  concentration of 0.5 to 2.0 ppm. The method of producing the electrolytic copper foil employs the copper electrolyte solution therefor.



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fig. 1

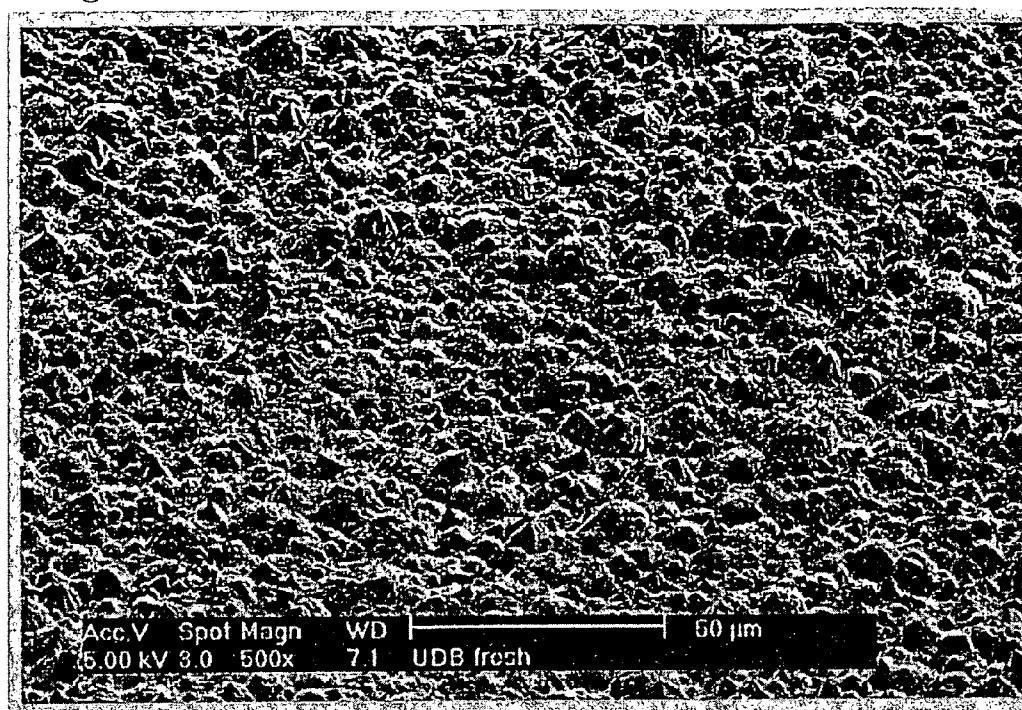
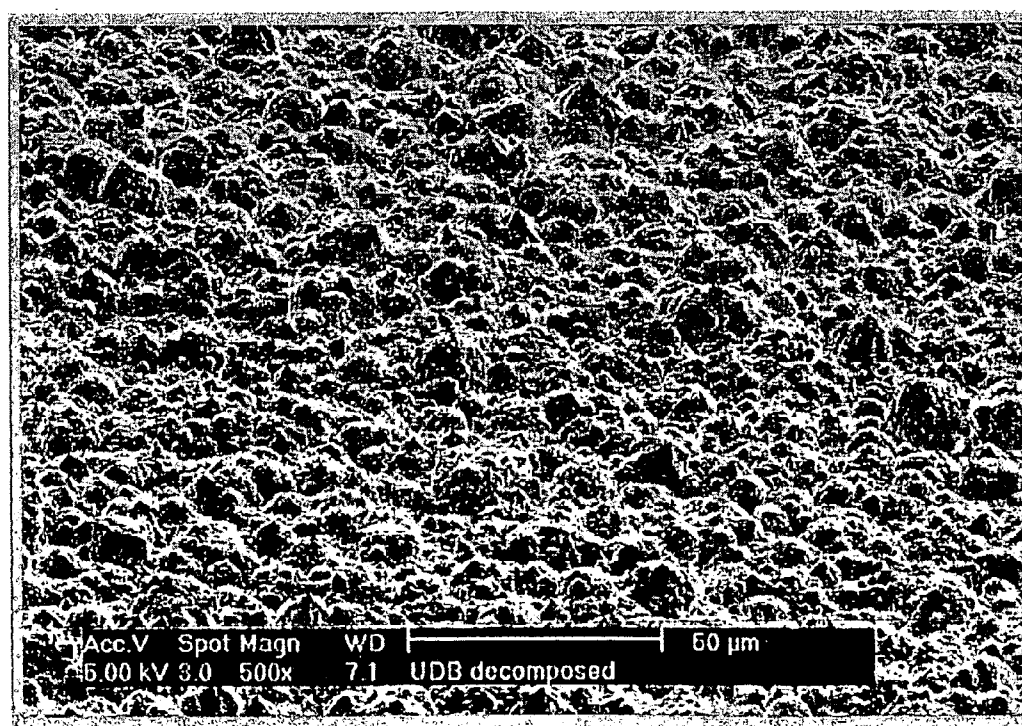
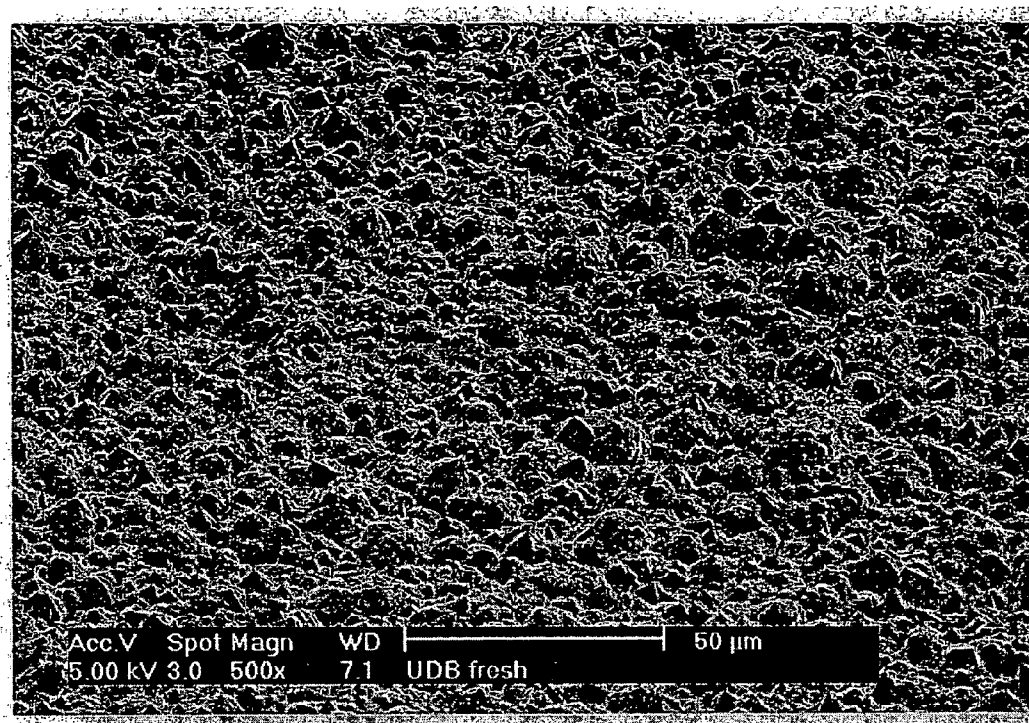


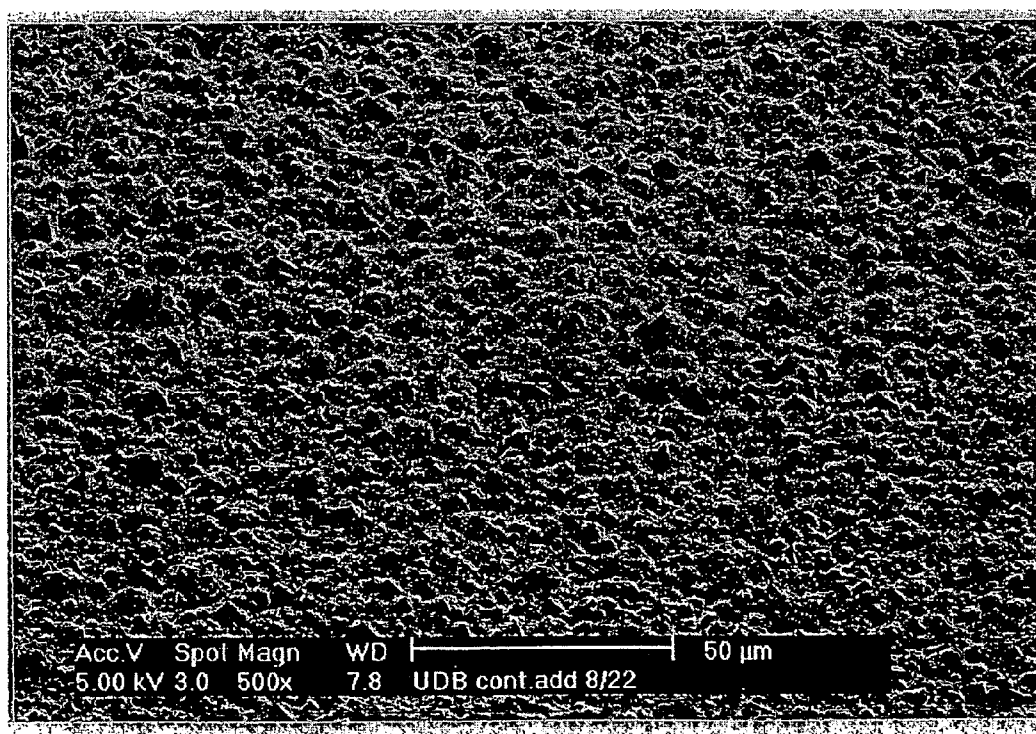
fig. 2



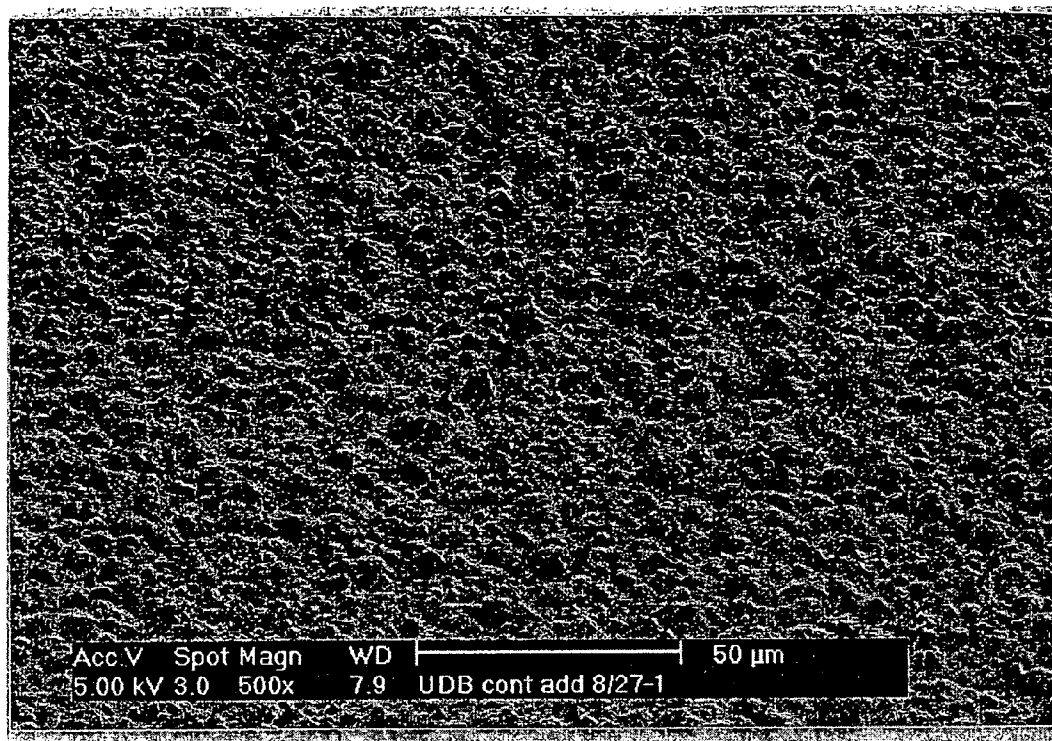
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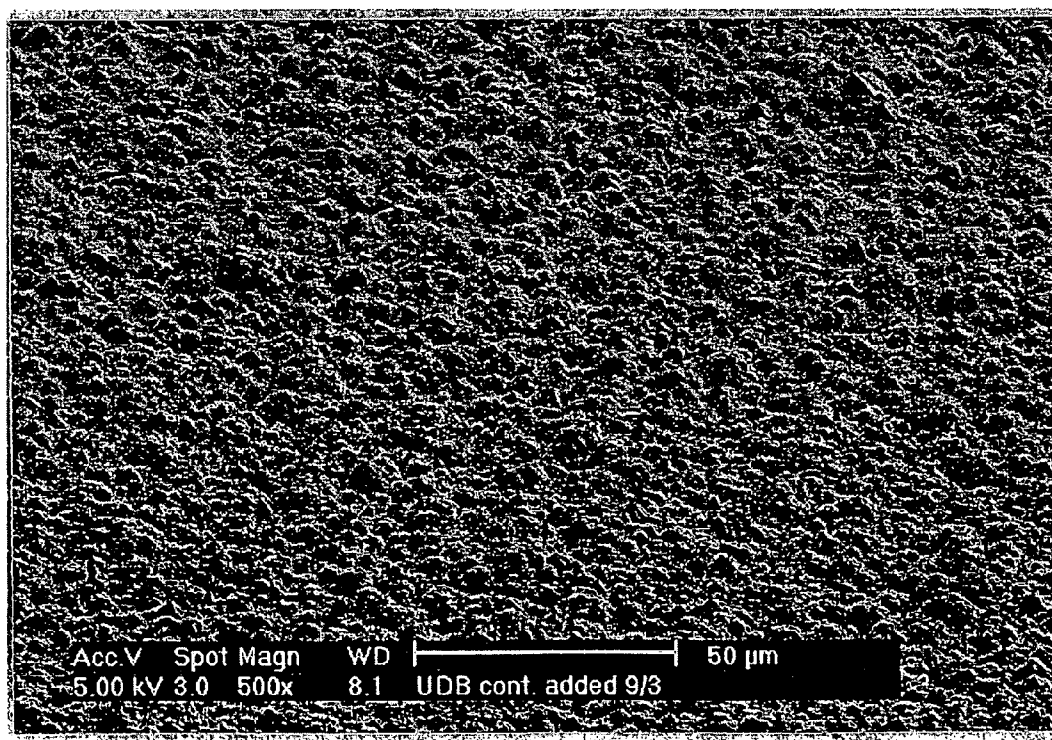
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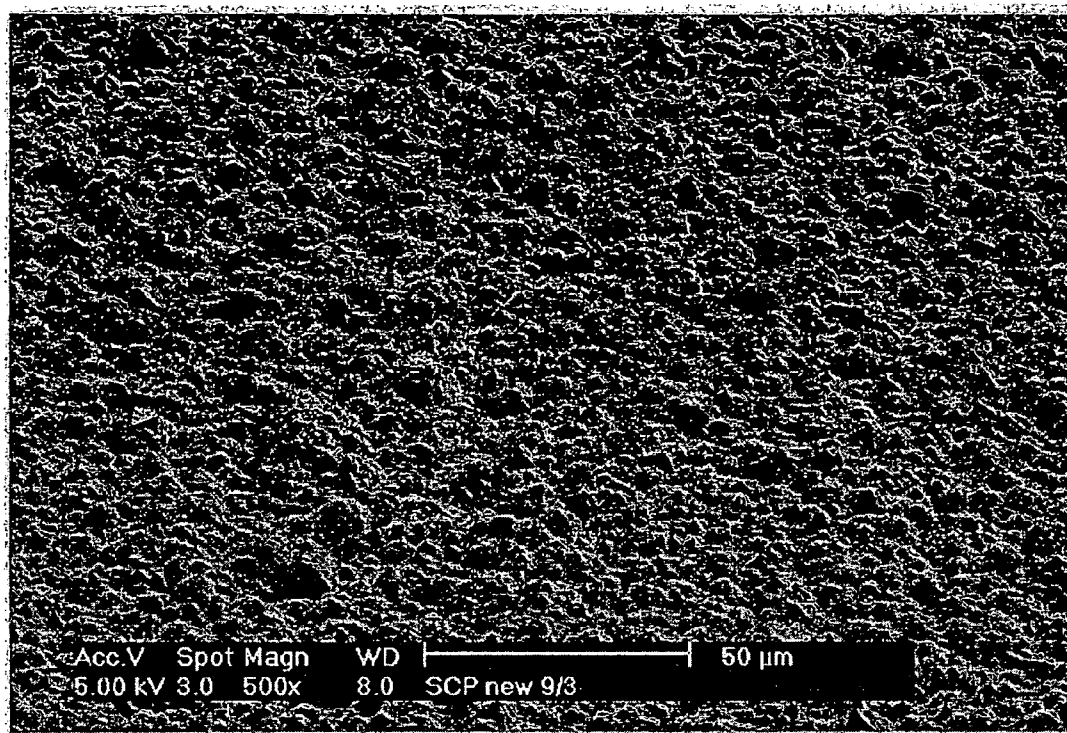
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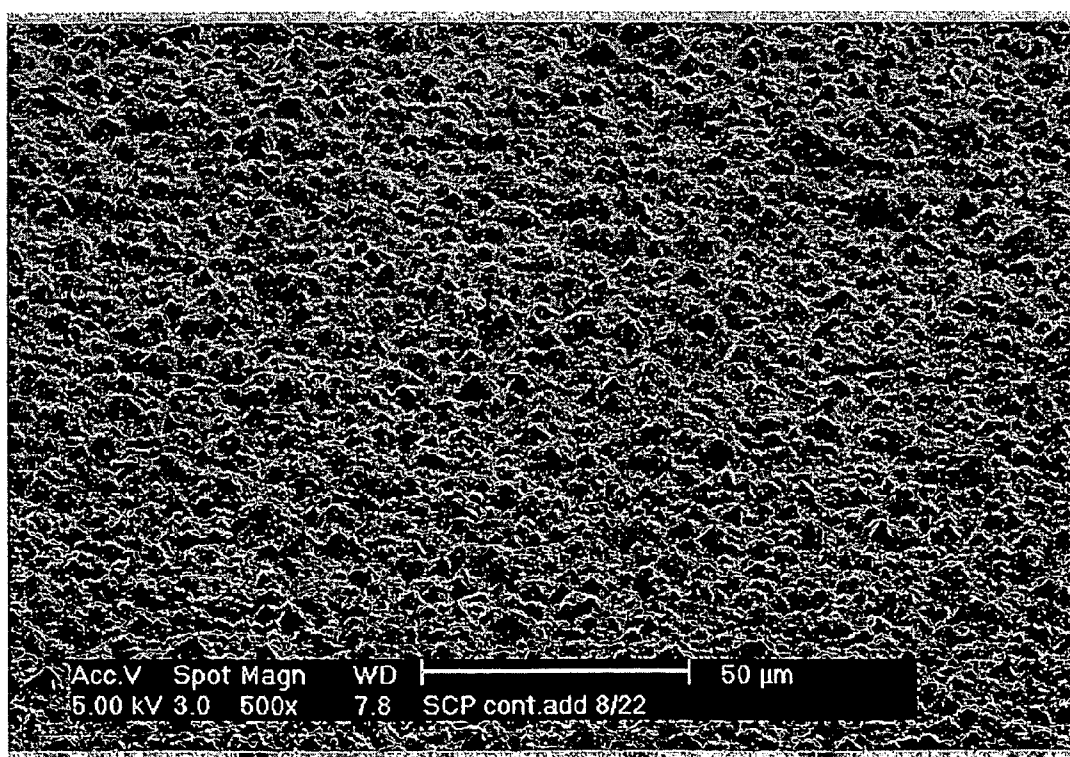
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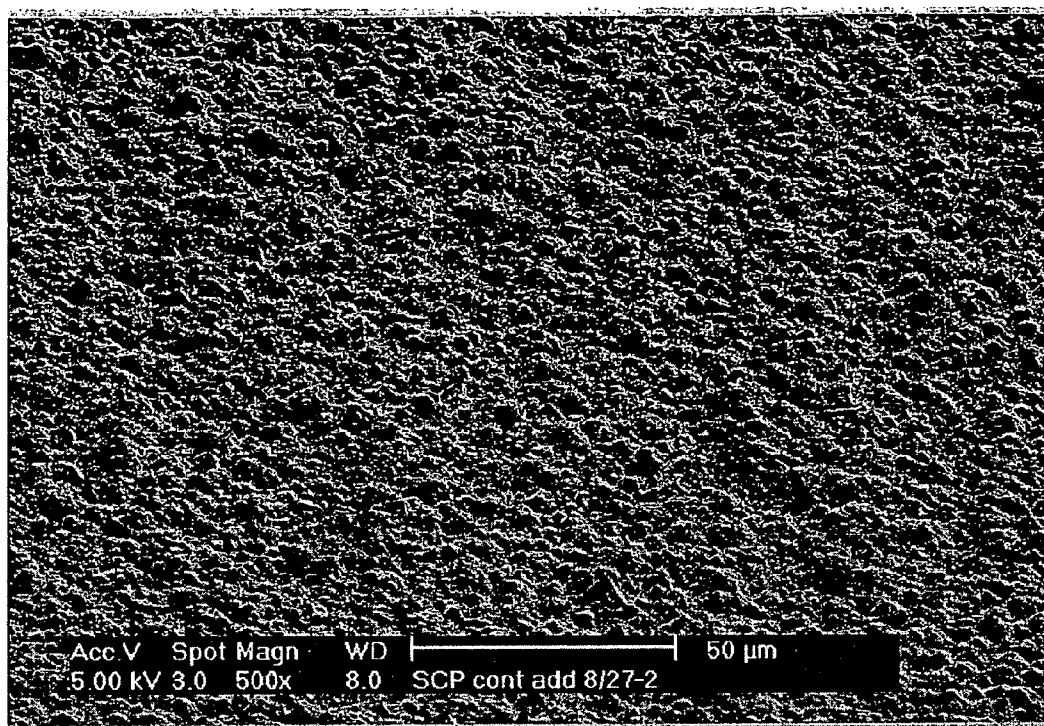
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f i g . 8



f i g. 9



f i g. 10

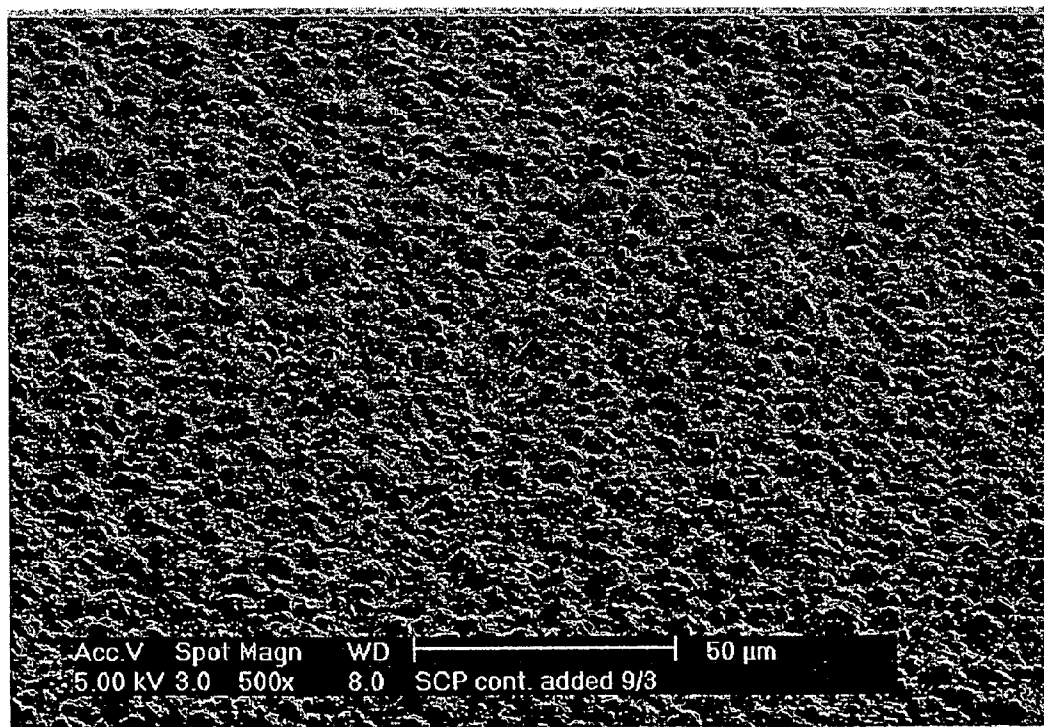




fig. 11

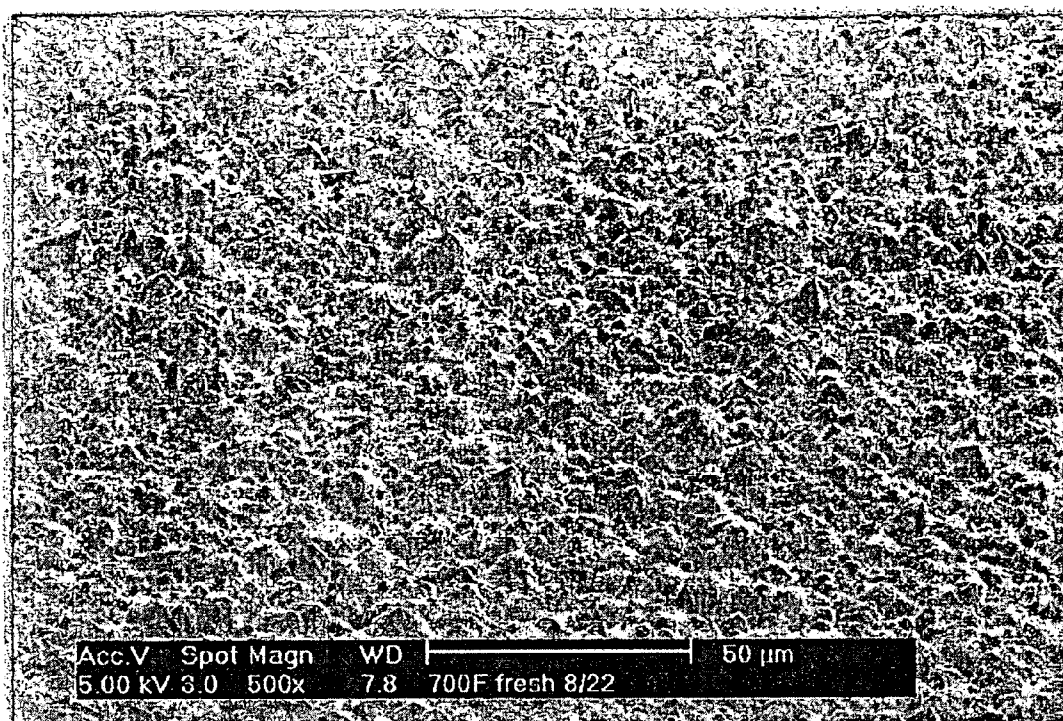
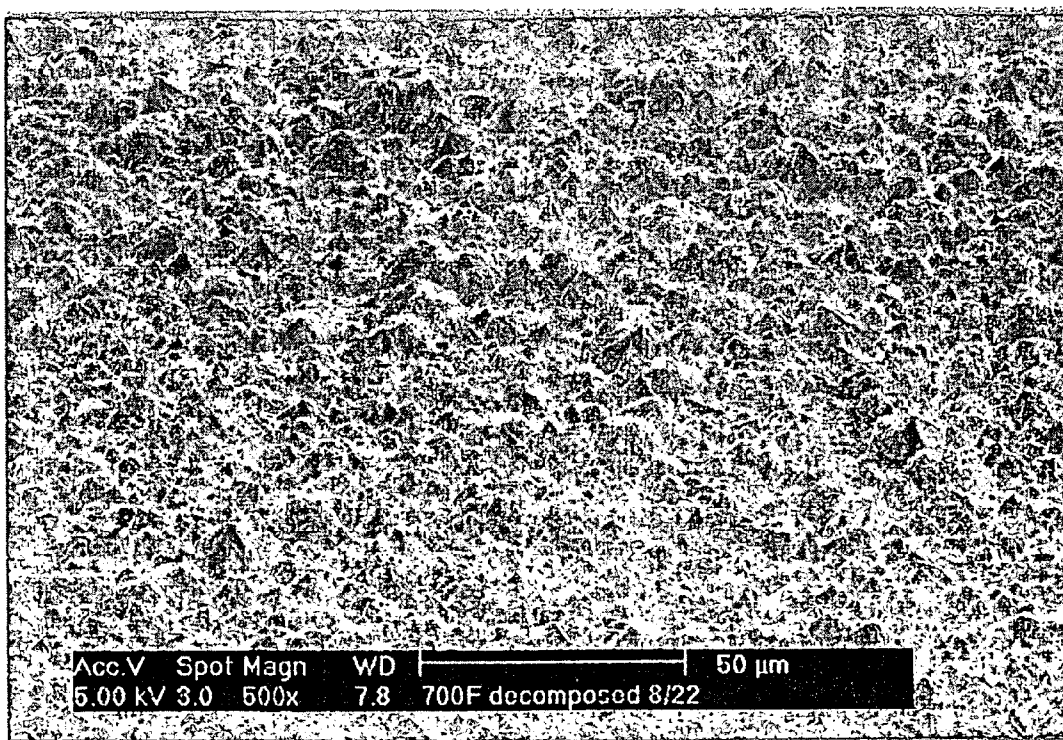
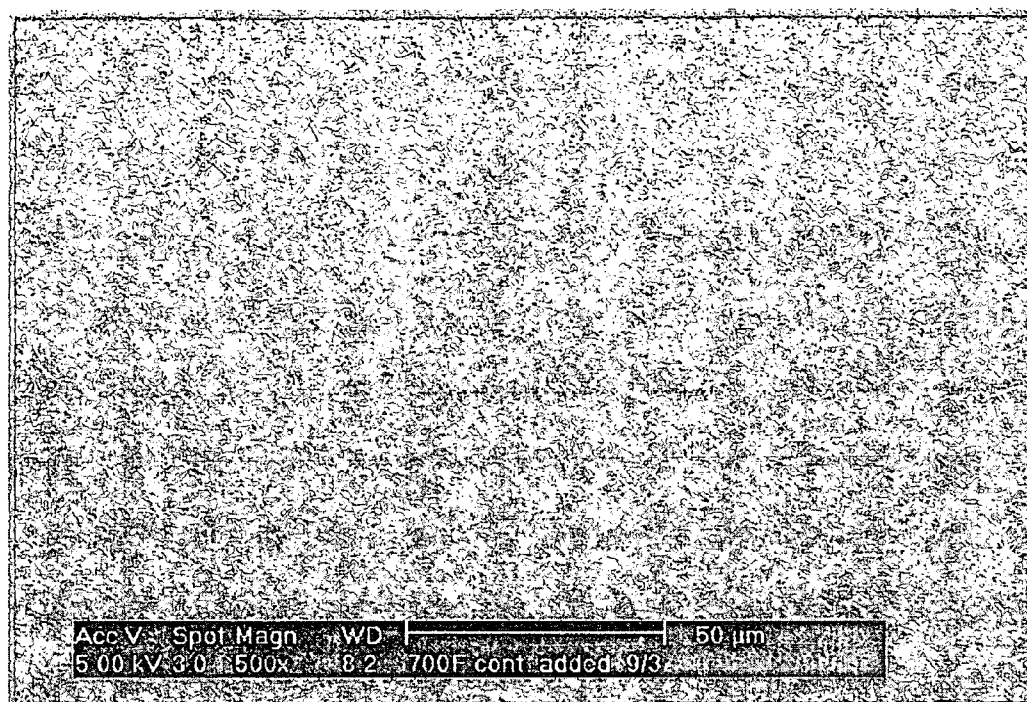


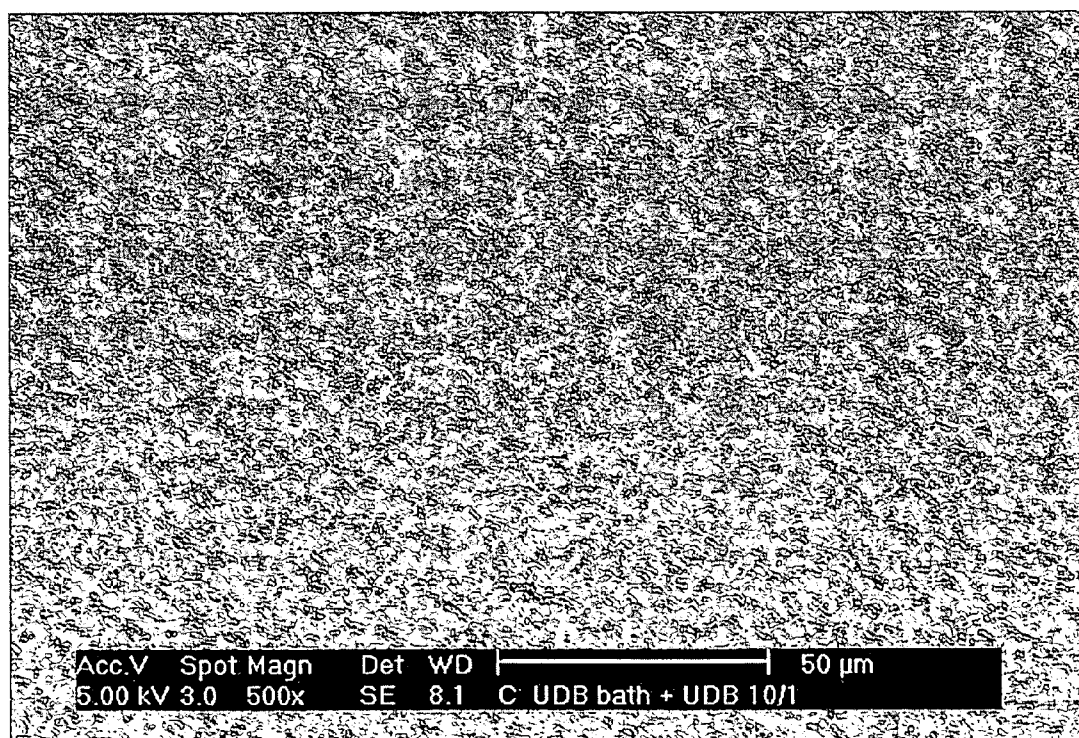
fig. 12



f i g. 1 3

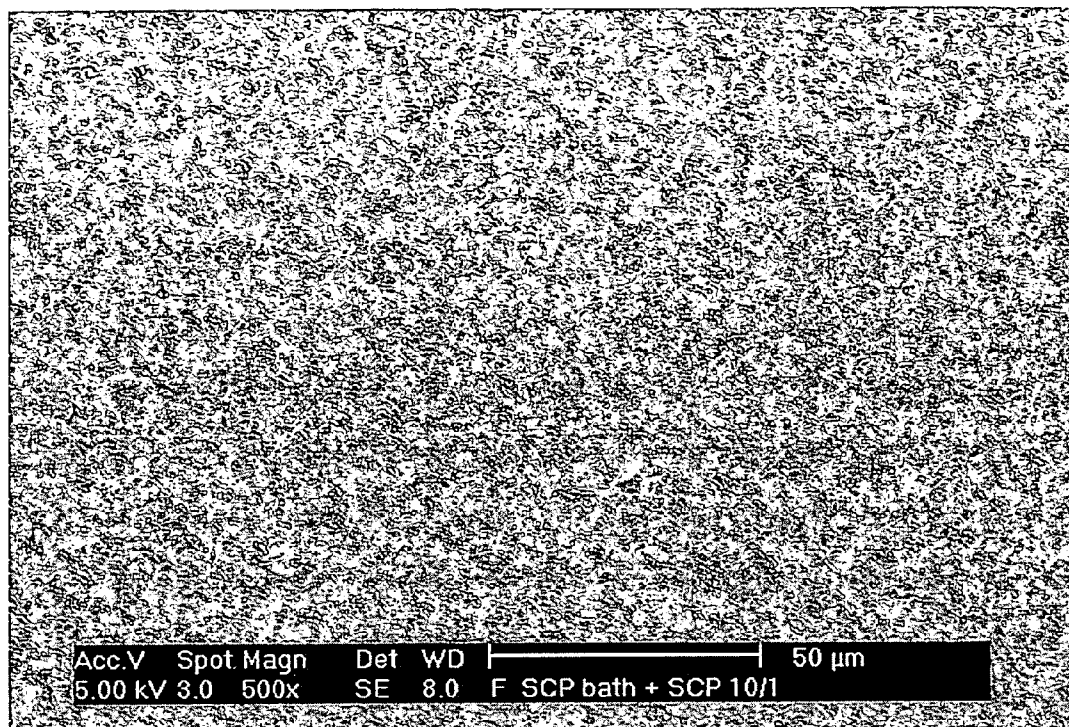


f i g. 1 4





f i g. 1 5



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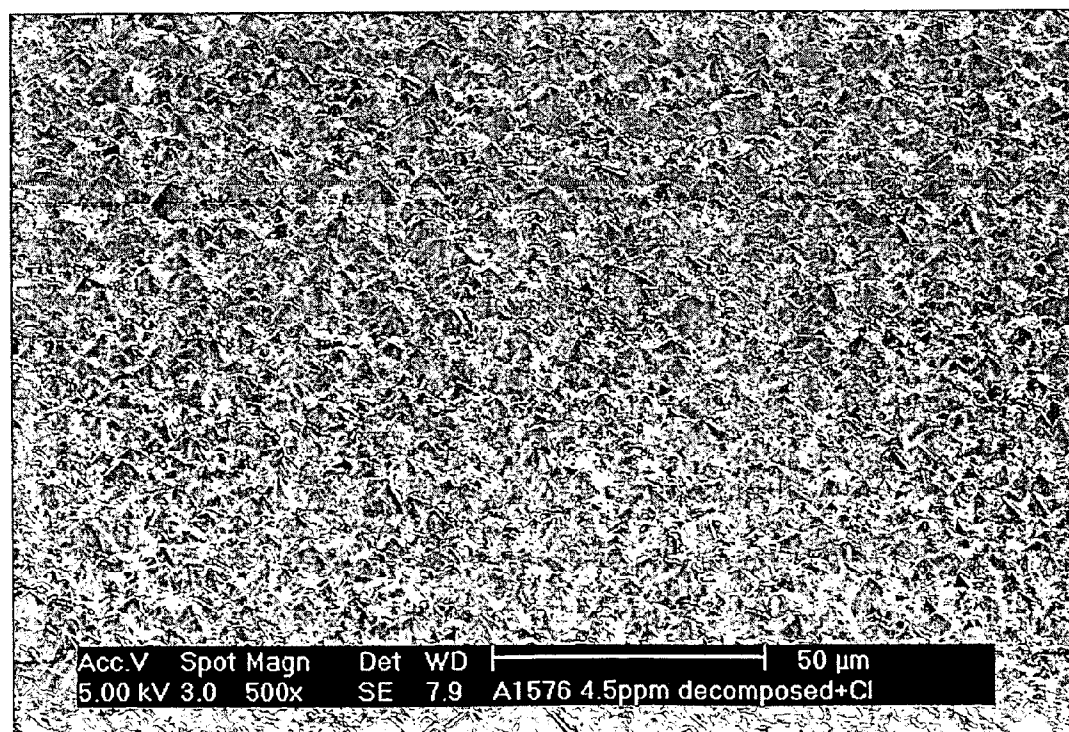


fig. 17

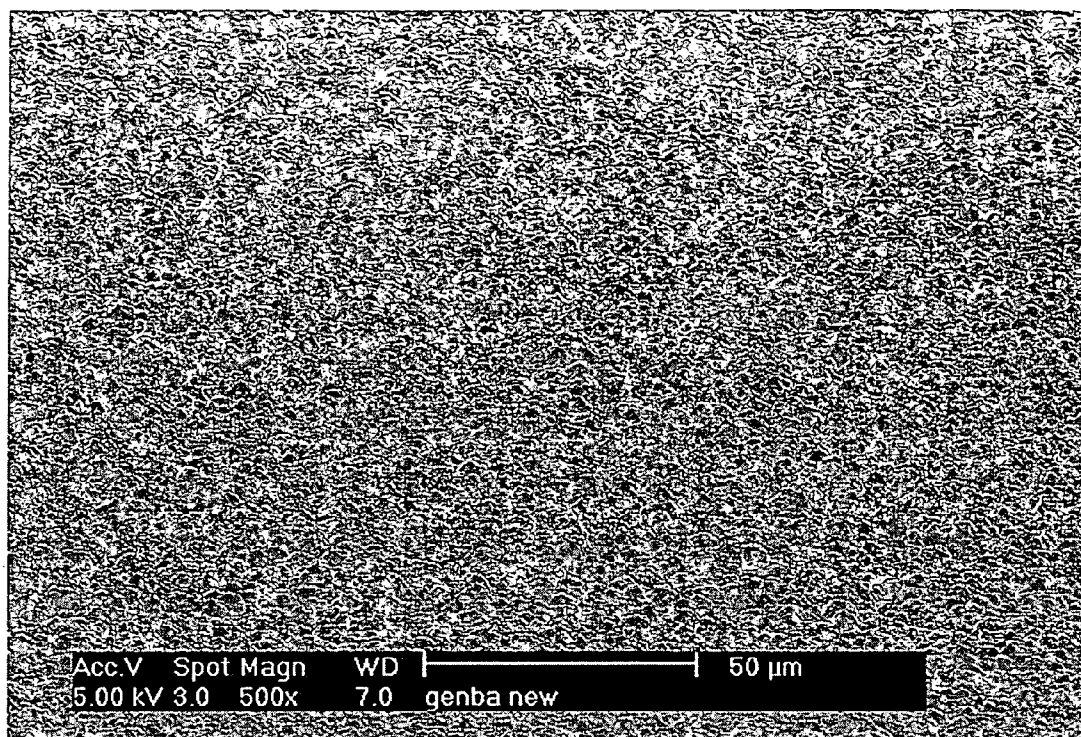


fig. 18

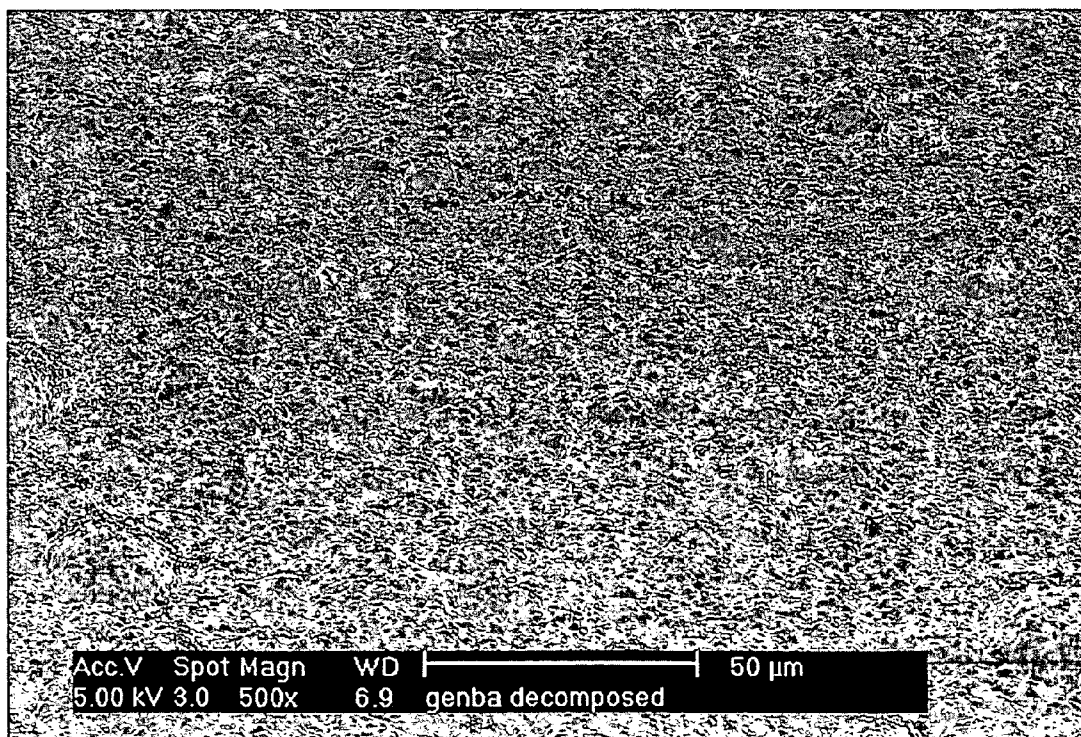


FIG. 19

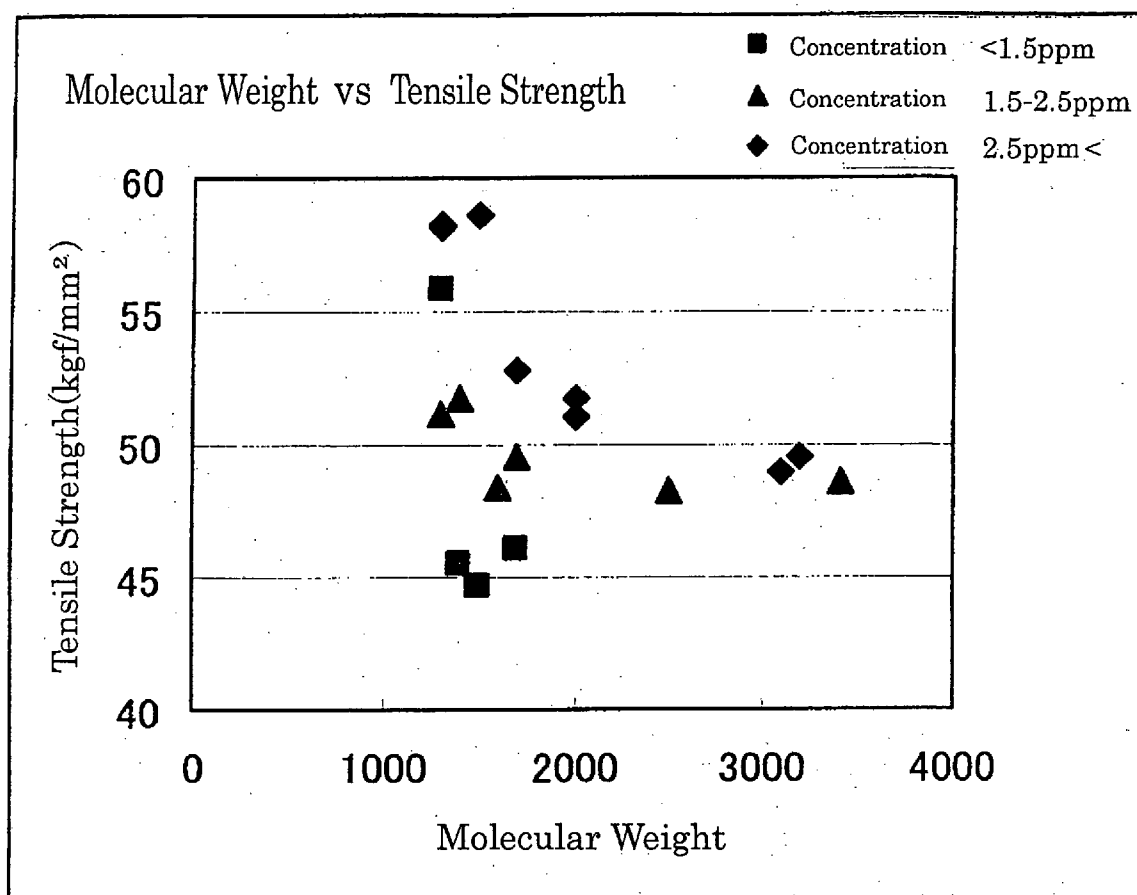
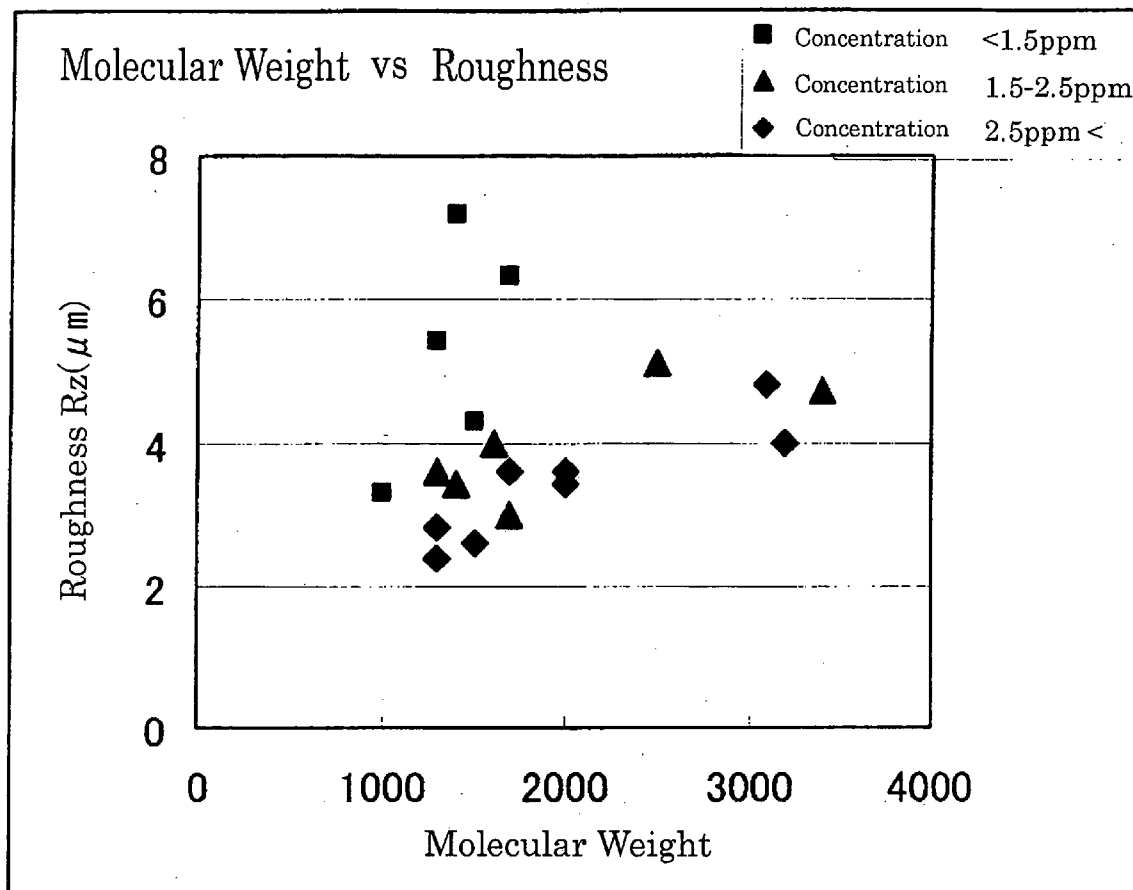
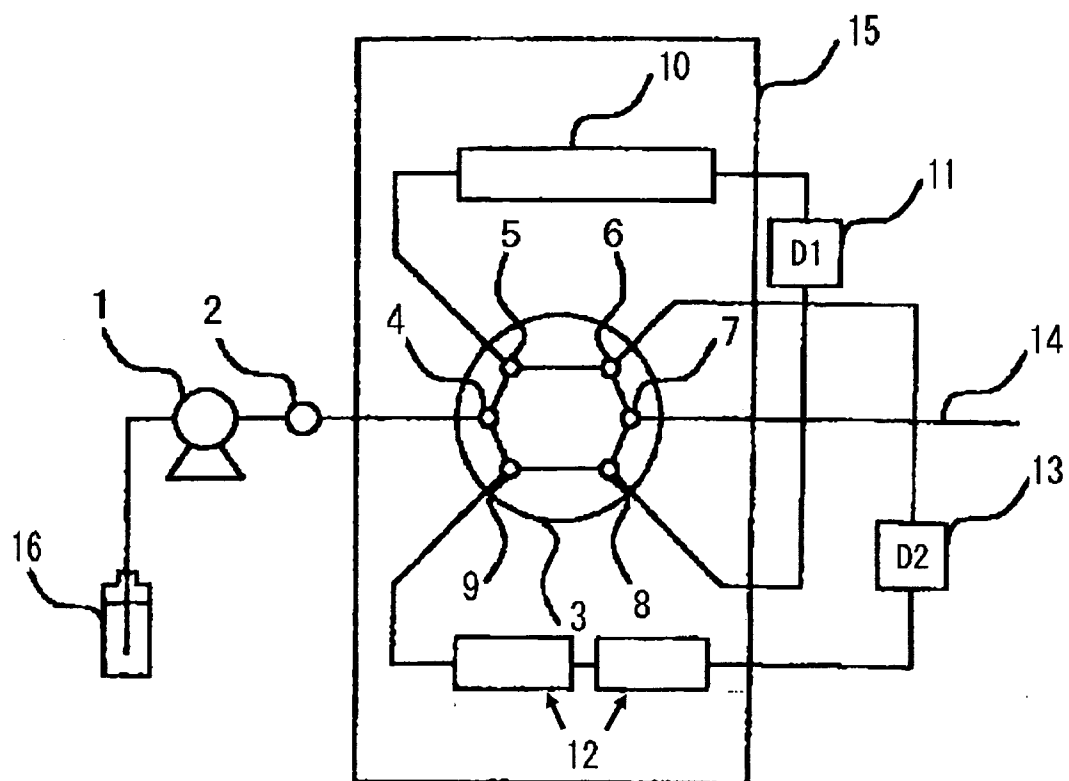


FIG. 20



f i g . 2 1





# **COPPER ELECTROLYSIS SOLUTION FOR PRODUCTION OF ELECTROLYTIC COPPER FOIL AND PROCESS FOR PRODUCING ELECTROLYTIC COPPER FOIL**

## **TECHNICAL FIELD**

[0001] The present invention relates to a copper electrolyte solution for producing an electrolytic copper foil and a method of producing the electrolytic copper foil, and more particularly relates to a copper electrolyte solution for producing an electrolytic copper foil in which the shape and the size of the mountain-shaped portions of the rough surface are uniform and which is suitable for producing a low roughness electrolytic copper foil, and a method of producing the electrolytic copper foil.

## **BACKGROUND ART**

[0002] Electrolytic copper foil means a foil (deposited foil) obtained by electrolytically depositing copper from a copper electrolyte solution containing copper ions to a cathode made of titanium and the like, or a foil (surface-treated foil) obtained by forming nodules or forming a metal layer or an organic component layer on the surface of the deposited foil, and these foils are being widely used as a material for fabricating a printed wiring board. Since deposited foil is obtained by electrolytic deposition on a cathode as described above, the cathode side (gloss surface, shiny surface or S surface) and the side opposite from the shiny surface (rough surface, mat surface or M surface) generally have different surface profiles and surface roughnesses. Specifically, the shiny surface of the deposited foil is generally smooth because the substantial profile of the cathode surface is substantially transferred thereto, while the rough surface has numerous mountain-shaped irregularities of a height (roughness) of about a few micrometers on the surface of copper grown upon electrolytic deposition. In addition, since the surface-treated foil is generally obtained by conducting surface treatment such as noduling substantially as it is without polishing the mountain-shaped irregularities of the rough surface of the deposited foil, the profile of the rough surface is greatly affected by the profile of the rough surface of the deposited foil. Accordingly, for electrolytic copper foil, controlling the shape and the size of the mountain-shaped irregularities (hereinafter sometimes simply referred to as "mountain") on the rough surface of the deposited foil is important.

[0003] When electrolytic copper foil is used as a material for fabricating a printed wiring board, high adhesion to other materials such as prepreg is required for the copper foil, and so a surface-treated foil with improved adhesion strength according to control of the surface profile is mainly used. However, since the surface profile of the surface-treated foil considerably retains the surface profile of the base deposited foil as described above, it is desired that the shape and the size of the mountain portions on the rough surface of the deposited foil are uniform for achieving stable properties such as adhesion strength and ensuring the insulating property upon lamination. On the other hand, for the demand of thinning of copper foil itself due to recent requirement of thinning of a printed wiring board, the surface-treated copper, or the rough surface of the deposited foil, is required to have small mountain roughness. Specifically, it is desired that the mountain roughness of the rough surface of the

deposited foil is not more than 4.2  $\mu\text{m}$  in  $R_z$  in the case of a deposited foil having a thickness of 35  $\mu\text{m}$ .

[0004] As a technique for making the shape of the mountain uniform and lowering the roughness of the rough surface of the deposited foil, various techniques such as control of the concentration of ions in a copper electrolyte solution have been disclosed in the past. Of these techniques, producing a deposited foil by electrolysis with continuously adding a predetermined amount of an aqueous solution (hereinafter also referred to as protein and the like-containing aqueous solution) in which protein and/or glue (hereinafter also referred to as protein and the like) are dissolved in a copper electrolyte solution is known to be a key factor for preparing a low roughness foil.

[0005] Specifically, the concentration and the molecular weight of protein and the like contained in a copper electrolyte solution are considered to have an influence on the shape of the mountain, the roughness and other properties of the rough surface of the deposited foil, and thus a method of measuring the concentration and the molecular weight of protein and the like contained in a copper electrolyte solution is known. In addition, it is known that protein and the like is decomposed by only leaving in a copper electrolyte solution to have a smaller molecular weight and that as it is consumed in the process of electrolysis, the concentration in the copper electrolyte solution is decreased.

[0006] It is noted that please refer to p. 2, column 1 of Japanese Patent Laid-Open No. 2001-337081.

[0007] However, for operation in factories, actual situation is that as a method of controlling the concentration and the molecular weight of protein, it is merely experimentally practiced that the initial molecular weight for preparing a protein and the like-containing aqueous solution is controlled by specifying the kind of protein to be dissolved, and the concentration in the copper electrolyte solution is controlled to a constant level by continuously adding thereto a predetermined amount of the protein and the like-containing aqueous solution. In short, in factory operation, without creating a steady state of continuously adding a predetermined amount of a protein and the like-containing aqueous solution using a specific kind of protein and the like, it becomes difficult to prepare a deposited foil having both low roughness and uniform shape and size of the mountains of the rough surface.

[0008] For example, when the time of adding or the amount of a protein and the like-containing aqueous solution upon electrolysis is incorrectly set or when a new copper electrolyte solution is to be prepared, in the former case, protein and the like are additionally added to cover the shortfall, but even if they are added, it is difficult to recover a good state, which is the steady state, of the mountain-shape and the roughness of the rough surface of the deposited foil to be obtained, i.e., uniform mountain-shapes and low roughness. Thus, there has been a problem that the yield of the deposited foil at this time is remarkably decreased. In the latter case, even if a protein and the like-containing aqueous solution is added under the conditions of the steady state of operation, a foil in which the mountain (peaks-and-troughs) shapes of the rough surface are uniform and which has a low roughness is difficult to obtain, and there has been a problem that the yield of the deposited foil at the initial stage of operation is remarkably decreased. There has also been a

problem that even if the same kind of protein is used, the mountain-shape of the M surface of the foil to be obtained varies only by a difference in the electrolysis production line.

[0009] In view of the above, an object of the present invention is to provide a copper electrolyte solution for producing an electrolytic copper foil, which can provide a deposited foil in which the shape and the size of mountain-shaped portions of the rough surface are uniform and which has low roughness, substantially without decrease of the yield of the deposited foil caused by control of the molecular weight and the concentration of protein and the like, and a method of producing an electrolytic copper foil using the same.

#### DISCLOSURE OF THE INVENTION

[0010] In view of such circumstances, the inventors of the present invention have conducted intensive studies and have found that, when a copper electrolyte solution for producing an electrolytic copper foil in which the number average molecular weight and the concentration of protein contained in the copper electrolyte solution are within specific ranges is used, the shape and the size of the mountains of the rough surface of the deposited foil become uniform and low roughness is achieved, and the present invention has been completed.

[0011] Accordingly, the present invention provides a copper electrolyte solution for producing an electrolytic copper foil, which contains protein having a number average molecular weight  $M_n$  of 1000 to 2300 at a concentration of 2 ppm to 4.5 ppm.

[0012] In the present invention, the copper electrolyte solution preferably has a  $\text{Cu}^{2+}$  concentration of 60 g/l to 100 g/L.

[0013] In the present invention, the copper electrolyte solution preferably has a free  $\text{SO}_4^{2-}$  concentration of 60 g/L to 250 g/L.

[0014] In the present invention, the copper electrolyte solution preferably has a  $\text{Cl}^-$  concentration of 0.5 ppm to 2.0 ppm.

[0015] In the present invention, the temperature of the copper electrolyte solution is preferably 40° C. to 60° C.

[0016] The present invention also provides a method of producing an electrolytic copper foil characterized by using the above-mentioned copper electrolyte solution for producing an electrolytic copper foil.

[0017] The present invention also provides a method of producing an electrolytic copper foil in which the current density for electrolysis is 30 A/cm<sup>2</sup> to 70 A/cm<sup>2</sup>.

[0018] According to the copper electrolyte solution for producing an electrolytic copper foil of the present invention, because the number average molecular weight  $M_n$  and the concentration of protein contained in the copper electrolyte solution are specified within the predetermined ranges upon electrolysis, a deposited foil in which the mountain-shapes of the rough surface are uniform and which has low roughness can be obtained. In addition, since protein is generally easily decomposed in a copper electrolyte solution, even protein having a number average molecular

weight  $M_n$  beyond the above-mentioned predetermined range can be used as a raw material, and thus the range of choices of available protein can be widened. Further, since the range to be controlled of the molecular weight and the concentration of protein for obtaining a deposited foil in which the mountain-shapes of the rough surface are uniform and which has low roughness has been clarified, a copper electrolyte solution suitable for producing a deposited foil in which the mountain-shapes of the rough surface are uniform and which has low roughness can be prepared in a short time, without limitation to the conventional, experimental standard steps of operation such as specifying the kind of protein to substantially control the initial number average molecular weight  $M_n$  thereof in a copper electrolyte solution, and adding a predetermined amount of an aqueous solution containing the protein to a copper electrolyte solution. Further, because a copper electrolyte solution can be prepared in such a short time, decrease in the yield of the deposited foil caused by control of protein in the copper electrolyte solution can be extremely small. In addition, because management of protein can be conducted only by setting the targets of the molecular weight and the concentration of protein in the electrolyte solution to predetermined management values, preparation of electrolyte solution in each production line is easy and the lines can be started faster. Moreover, according to the method of producing an electrolytic copper foil of the present invention, by using the above-mentioned copper electrolyte solution, a deposited foil in which the mountain-shapes of the rough surface are uniform and which has low roughness can be obtained.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1 is an SEM micrograph of the rough surface of the foil obtained in Comparative Example 1;

[0020] FIG. 2 is an SEM micrograph of the rough surface of the foil obtained in Comparative Example 2;

[0021] FIG. 3 is an SEM micrograph of the rough surface of the foil obtained in Comparative Example 3;

[0022] FIG. 4 is an SEM micrograph of the rough surface of the foil obtained in Example 1;

[0023] FIG. 5 is an SEM micrograph of the rough surface of the foil obtained in Example 2;

[0024] FIG. 6 is an SEM micrograph of the rough surface of the foil obtained in Example 3;

[0025] FIG. 7 is an SEM micrograph of the rough surface of the foil obtained in Comparative Example 4;

[0026] FIG. 8 is an SEM micrograph of the rough surface of the foil obtained in Example 4;

[0027] FIG. 9 is an SEM micrograph of the rough surface of the foil obtained in Example 5;

[0028] FIG. 10 is an SEM micrograph of the rough surface of the foil obtained in Example 6;

[0029] FIG. 11 is an SEM micrograph of the rough surface of the foil obtained in Comparative Example 5;

[0030] FIG. 12 is an SEM micrograph of the rough surface of the foil obtained in Comparative Example 6;

[0031] FIG. 13 is an SEM micrograph of the rough surface of the foil obtained in Example 7;

[0032] FIG. 14 is an SEM micrograph of the rough surface of the foil obtained in Example 8;

[0033] FIG. 15 is an SEM micrograph of the rough surface of the foil obtained in Example 9;

[0034] FIG. 16 is an SEM micrograph of the rough surface of the foil obtained in Comparative Example 8;

[0035] FIG. 17 is an SEM micrograph of the rough surface of the foil obtained in Example 10;

[0036] FIG. 18 is an SEM micrograph of the rough surface of the foil obtained in Comparative Example 9;

[0037] FIG. 19 is a graph showing the relation between the number average molecular weight  $M_n$  and the concentration of protein contained in copper electrolyte solutions, and the tensile strength of deposited foils in an ordinary state;

[0038] FIG. 20 is a graph showing the relation between the number average molecular weight  $M_n$  and the concentration of protein contained in copper electrolyte solutions, and the roughness  $R_z$  of the rough surface of deposited foils; and

[0039] FIG. 21 is a schematic view illustrating an example of an apparatus used in the method of measuring the number average molecular weight  $M_n$  and the concentration of protein in the present invention.

#### DESCRIPTION OF SYMBOLS

- [0040] 1 liquid supply pump
- [0041] 2 injector
- [0042] 3 6-ways-direction switching valve
- [0043] 4 first connecting port of 6-ways-direction switching valve
- [0044] 5 second connecting port of 6-ways-direction switching valve
- [0045] 6 third connecting port of 6-ways-direction switching valve
- [0046] 7 fourth connecting port 6-ways-direction switching valve
- [0047] 8 fifth connecting port of 6-ways-direction switching valve
- [0048] 9 sixth connecting port of 6-ways-direction switching valve
- [0049] 10 pre-treatment column
- [0050] 11 first detector
- [0051] 12 separation column
- [0052] 13 second detector
- [0053] 14 drain pipe
- [0054] 15 constant-temperature bath
- [0055] 16 mobile phase reservoir

#### BEST MODE FOR CARRYING OUT THE INVENTION

(Copper Electrolyte Solution for Producing Electrolytic Copper Foil of the Present Invention)

[0056] The copper electrolyte solution for producing an electrolytic copper foil of the present invention is used for producing an electrolytic copper foil. The copper electrolyte solution may be an electrolyzable solution containing copper ions ( $\text{Cu}^{2+}$ ), and for example, an acid bath may be used. As the acid bath, for example, a sulfuric acid bath may be used. The sulfuric acid bath is preferable because it affords excellent properties of the obtained deposited foil, its waste water can be easily processed and it can easily dissolve copper wire which is a raw material of a copper electrolyte solution.

[0057] The above-mentioned copper electrolyte solution has  $\text{Cu}^{2+}$  concentration of usually 60 g/L to 100 g/L, preferably 70 g/L to 90 g/L.  $\text{Cu}^{2+}$  concentration of lower than 60 g/L is not preferable because the solution resistance is increased.  $\text{Cu}^{2+}$  concentration of higher than 100 g/L is not preferable because crystal of copper sulfate tends to precipitate.

[0058] When a sulfuric acid bath is used for the above-mentioned copper electrolyte solution, the free  $\text{SO}_4^{2-}$ -concentration is usually 60 g/L to 250 g/L, preferably 100 g/L to 200 g/L. Herein, the free  $\text{SO}_4^{2-}$ -concentration refers to the concentration of remaining  $\text{SO}_4^{2-}$ -found by subtracting the  $\text{SO}_4^{2-}$ -concentration calculated from conversion of the  $\text{Cu}^{2+}$  concentration in the copper electrolyte solution to  $\text{CuSO}_4$  from the total  $\text{SO}_4^{2-}$ -concentration in the copper electrolyte solution. Free  $\text{SO}_4^{2-}$ -concentration of lower than 60 g/L is not preferable because the solution resistance is increased. Free  $\text{SO}_4^{2-}$ -concentration of higher than 250 g/L is not preferable because extraordinary deposition tends to occur in the deposited foil. In the present invention, the deposited foil means a copper foil obtained by electrolytically depositing copper from a copper electrolyte solution containing copper ions to a cathode made of titanium and the like, which is a copper foil without surface treatment such as nodule-producing treatment, i.e., non surface-treated copper foil.

[0059] The above-mentioned copper electrolyte solution has a  $\text{Cl}^-$  concentration of usually 0.5 ppm to 2.0 ppm, preferably 1.5 ppm to 1.9 ppm. As used herein, ppm represents mg/L.  $\text{Cl}^-$  concentration of lower than 0.5 ppm is not preferable because the mountain-shape relative to the protein concentration in the present invention is not excellent.  $\text{Cl}^-$ -concentration of higher than 2.0 ppm is not preferable because microporosities tend to be generated in the deposited foil. In the present invention, when the concentration and the molecular weight of protein and the  $\text{Cl}^-$ -concentration are each within the predetermined ranges as described above, the mountain-shape of the deposited foil is excellent. This suggests that for controlling the mountain-shape of the deposited foil, there is some correlation between the concentration and molecular weight of protein and the  $\text{Cl}^-$ -concentration.

[0060] The above-mentioned copper electrolyte solution contains protein. Examples of protein include gelatin, glue or the like. In order to add protein to a copper electrolyte solution, usually protein is dissolved in water and the aqueous protein solution is added to the copper electrolyte solution. As a raw material protein for preparing such

aqueous protein solution, protein having a number average molecular weight  $M_n$  of not less than 1700 is used. This is because the number average molecular weight  $M_n$  of protein is decreased because protein is decomposed in the copper electrolyte solution or the aqueous solution, and to set the number average molecular weight  $M_n$  in the copper electrolyte solution to 1000 to 2300 as described later, the number average molecular weight is preferably slightly higher than the lower limit in consideration of the decomposition.

[0061] The raw material protein may be, for example, protein of which the number average molecular weight  $M_n$  in the copper electrolyte solution can be set within the above-mentioned range, and is thus not particularly limited. For example, DVM80 available from Asahi Gelatine Industrial Co., Ltd, UDB available from Nitta Gelatin Inc., SCP5000 available from Nitta Gelatin Inc. and 700F available from Nitta Gelatin Inc. may be used.

[0062] The protein contained in the above-mentioned copper electrolyte solution has a number average molecular weight  $M_n$  of usually 1000 to 2300, preferably 1200 to 2100, and the concentration of the protein in the solution is usually 2 ppm to 4.5 ppm, preferably 2.0 ppm to 3.6 ppm, more preferably more than 2.5 ppm to not more than 3.6 ppm. A number average molecular weight  $M_n$  and a concentration of protein in the copper electrolyte solution within the above-mentioned range are preferable, because a deposited foil in which the shape and the size of the mountains of the rough surface are uniform and which has low roughness can be obtained. In the present invention, the number average molecular weight  $M_n$  and the concentration of protein refer to the number average molecular weight  $M_n$  and the concentration of protein which has a number average molecular weight  $M_n$  of not less than 790.

[0063] Here, FIG. 19 shows the relation between the number average molecular weight  $M_n$  and the concentration of protein contained in the above-mentioned copper electrolyte solution and the tensile strength of the deposited foil in an ordinary state. FIG. 20 shows the relation between the number average molecular weight  $M_n$  and the concentration of protein contained in the above-mentioned copper electrolyte solution and the roughness  $R_z$  of the rough surface of the deposited foil. In FIG. 19, the X-axis indicates the number average molecular weight  $M_n$  of protein contained in the copper electrolyte solution and the Y-axis indicates the tensile strength of the deposited foil in an ordinary state. In FIG. 20, the X-axis indicates the number average molecular weight  $M_n$  of protein contained in the copper electrolyte solution and the Y-axis indicates the roughness  $R_z$  of the rough surface of the deposited foil.

[0064] In FIGS. 19 and 20, samples having a protein concentration in a copper electrolyte solution of less than 1.5 ppm are indicated by square plots (hereinafter referred to as plot A, the group constituted by plots A referred to as plot A group), samples of 1.5 ppm to 2.5 ppm are indicated by triangle plots (hereinafter referred to as plot B, the group constituted by plots B referred to as plot B group) and samples of more than 2.5 ppm are indicated by diamond plots (hereinafter referred to as plot C, the group constituted by plots C referred to as plot C group).

[0065] From FIGS. 19 and 20, comparison between the plot A group, the plot B group and the plot C group shows a tendency that when the concentrations of protein contained

in the copper electrolyte solution are about the same, the smaller the number average molecular weight  $M_n$  of the protein contained in the copper electrolyte solution, the higher the tensile strength in an ordinary state of the deposited foil and the smaller the roughness  $R_z$ . Another comparison between the plot A group, the plot B group and the plot C group shows a tendency that when the number average molecular weights  $M_n$  of protein contained in the copper electrolyte solution are about the same, the higher the concentration of the protein contained in the copper electrolyte solution, the higher the tensile strength in an ordinary state of the deposited foil and the smaller the roughness  $R_z$ . This shows that the smaller the number average molecular weight  $M_n$  of the protein and the higher the concentration of the protein, the higher the tensile strength in an ordinary state of the deposited foil and the smaller the roughness  $R_z$ .

[0066] As described above, a smaller number average molecular weight  $M_n$  and a higher concentration are preferable because the tensile strength of the deposited foil in an ordinary state is higher and the roughness  $R_z$  is smaller. On the other hand, however, when the concentration of protein is too high, there is an undesirable problem that the viscosity of the copper electrolyte solution becomes too high and foaming tends to occur. When the number average molecular weight  $M_n$  of protein is too small, there is an undesirable problem that the concentration of necessary protein in the copper electrolyte solution becomes higher, the viscosity of the copper electrolyte solution becomes too high as described above, and foaming tends to occur. For these reasons, the present invention defines the lower limit of the number average molecular weight  $M_n$  of protein and the upper limit of the concentration of protein as described above.

[0067] Moreover, regarding the degree of the increase of the tensile strength in an ordinary state of the deposited foil relative to the decrease of the number average molecular weight  $M_n$  of protein contained in the copper electrolyte solution, i.e., the gradient of each of the plot A group, the plot B group and the plot C group against the X-axis (number average molecular weight  $M_n$  of protein) in FIG. 19, it is found that in the order of the gradient of plot A group, the gradient of the plot B group and the gradient of the plot C group, the first one has a greater degree of decrease of the gradient while the last one has a smaller degree of decrease of the gradient, with the gradient approaching horizontal. This shows that the higher the concentration of the protein in the copper electrolyte solution, the slower the change in the tensile strength in an ordinary state of the deposited foil relative to the change in the number average molecular weight  $M_n$  of the protein, and the smaller the dispersion of the tensile strength in an ordinary state of the deposited foil caused by the change in the concentration of the protein in the copper electrolyte solution. On the other hand, it is found that the lower the concentration of the protein in the copper electrolyte solution, the sharper the change in the tensile strength in an ordinary state of the deposited foil relative to the change in the number average molecular weight  $M_n$  of the protein, and the greater the dispersion of the tensile strength in an ordinary state of the deposited foil caused by the change in the concentration of the protein in the copper electrolyte solution.

[0068] Regarding the degree of the decrease of the roughness  $R_z$ , relative to the decrease of the number average molecular weight  $M_n$  of protein contained in the copper electrolyte solution, i.e., the gradient of each of the plot A group, the plot B group and the plot C group against the X-axis (number average molecular weight  $M_n$  of protein) in FIG. 20, it is found that in the order of the gradient of plot A group, the gradient of the plot B group and the gradient of the plot C group, the first one has a greater degree of increase of the gradient while the last one has a smaller degree of increase of the gradient, with the gradient approaching horizontal. This shows that the higher the concentration of the protein in the copper electrolyte solution, the slower the change in the roughness  $R_z$  relative to the change in the number average molecular weight  $M_n$  of the protein, and the smaller the dispersion of the roughness  $R_z$  caused by the change in the concentration of the protein in the copper electrolyte solution. On the other hand, it is found that the lower the concentration of the protein in the copper electrolyte solution, the sharper the change in the roughness  $R_z$  relative to the change in the number average molecular weight  $M_n$  of the protein, and the greater the dispersion of the roughness  $R_z$  caused by the change in the concentration of the protein in the copper electrolyte solution.

[0069] The method of measuring the number average molecular weight  $M_n$  and the concentration of protein contained in the copper electrolyte solution is now described. For the measuring method, a method described in Japanese Patent Laid-Open No. 2001-337081 may be employed. Specifically, a method of measuring the concentration and the molecular weight distribution of protein according to high performance liquid chromatography, preferably gel permeation chromatography combined with a column switching method is used. In this measuring method, a mixed solution of not less than 3% by volume of acetonitrile and not more than 97% by volume of diluted sulfuric acid having a concentration of 0.002 M to 0.01 M may be used as a mobile phase, a filler with a size exclusion mode of an molecular weight exclusion limit of not more than 2500 may be used as a filler for a pre-treatment column, a filler with a size exclusion mode of an molecular weight exclusion limit of not less than 10000 may be used as a filler for a separation column, and for the separation column, two or more columns connected in series are preferable. By using the above-mentioned measuring method, the molecular weight distribution and the concentration of protein contained in the copper electrolyte solution are measured, and the number average molecular weight  $M_n$  is calculated based on the molecular weight distribution.

[0070] The method of measuring the number average molecular weight  $M_n$  and the concentration of protein is described in detail referring to Figures. FIG. 21 is a schematic view illustrating an example of an apparatus used in the method of measuring the number average molecular weight  $M_n$  and the concentration of protein in the present invention. The apparatus illustrated in FIG. 21 is equipped with a liquid supply pump 1, a 6-ways-direction switching valve 3, an injector 2 interconnected between the liquid supply pump 1 and a first connecting port 4 of the 6-ways-direction switching valve 3, a pre-treatment column 10 interconnected to a second connecting port 5 of the switching valve, a first detector 11 interconnected between the pre-treatment column 10 and the fifth connecting port 8 of the switching valve, two separation columns 12 and 12

interconnected in series to a sixth connecting port 9 of the switching valve, a second detector 13 interconnected between the separation columns 12 and a third connecting port 6 of the switching valve, a data processing unit (not represented in the figure) for calculating the concentration and the molecular weight distribution of protein based on the data detected in the second detector 13, a drain pipe 14 interconnected to a fourth connecting port 7 of the switching valve, and a constant-temperature bath 15 for maintaining the pre-treatment column and the separation columns at a constant temperature. For piping, tube made of preferably PEEK® or Teflon® is used.

[0071] For the detectors 11 and 13, detectors generally used for high performance liquid chromatography, which can detect protein of mg/L level, e.g. a spectrophotometric detector may be used. In addition, in the present invention, any data processing unit that has a computational capability to calculate the concentration and the molecular weight distribution of protein based on the data detected in the detectors 11 and 13 may be used.

[0072] Upon measurement using such measuring apparatus as described above, the 6-ways-direction switching valve 3 first allows communication between the first connecting port 4 and the second connecting port 5, between the fifth connecting port 8 and the sixth connecting port 9, and between the third connecting port 6 and the fourth connecting port 7. With such configuration, for example, mobile phase of a mixed solution of 0.005 M sulfuric acid and acetonitrile in a volume ratio of 95 to 5 is made to flow via the liquid supply pump 1, at a constant flow rate, in the order of a mobile phase reservoir 16→liquid supply pump 1→injector 2→6-ways-direction switching valve 3→pre-treatment column 10→first detector 11→6-ways-direction switching valve 3→separation columns 12, 12→second detector 13→6-ways-direction switching valve 3→drain pipe 14. With such settings, 200  $\mu$ l of a protein-containing electrolyte solution as is or 200  $\mu$ l of a sample diluted with pure water is introduced to the injector 2. The electrolyte solution is poured into a pre-treatment column 10 filled with an aqueous size exclusion mode filler having a molecular weight exclusion limit of not more than 2500, for example, a PEEK® column 7.5 mm in inner diameter and 250 mm in length, packed with Sephadex G-15 available from Amersham Pharmacia Biotech AB (molecular weight exclusion limit 1500). The electrolyte solution entered into the pre-treatment column 10 is separated according to the separation mechanism of size exclusion chromatography, and protein having a larger molecular weight is first eluted and electrolyte solution components which are low molecular weight substances are then eluted.

[0073] The protein and the electrolyte solution components eluted through the pre-treatment column 10 are monitored in the first detector 11, e.g., a spectrophotometric detector, at a measurement wavelength of 210 nm. After the protein is introduced into the separation columns 12 and 12 but before large amounts of electrolyte solution components are introduced to the separation columns 12 and 12, the 6-ways-direction switching valve is switched to allow communication between the first connecting port 4 and the sixth connecting port 9, between the third connecting port 6 and the second connecting port 5, and between the fifth connecting port 8 and the fourth connecting port 7. With these settings, the mobile phase flows through the mobile phase



reservoir 16→liquid supply pump 1→injector 2→6-ways-direction switching valve 3→separation columns 12, 12→second detector 13→6-ways-direction switching valve 3→pre-treatment column 10→first detector 11→6-ways-direction switching valve 3→drain pipe 14 to discharge the electrolyte solution components outside the system via the drain pipe 14. In this regard, when the above-mentioned method of measuring the concentration and the molecular weight distribution of protein is employed, measurement of protein having a molecular weight of 790 or more is generally possible, and thus when switching the 6-ways-direction switching valve, attention should be paid to avoid excluding proteins having a molecular weight of 790 or more from the system.

[0074] The protein introduced into the separation column 12 is separated and eluted according to the molecular weight and the molecular weight distribution. The eluted protein is detected in the second detector, e.g., a spectrophotometric detector at a measurement wavelength of 210 nm and based on the detected data, the concentration and the molecular weight distribution of the protein are calculated by the data processing unit.

[0075] In the above-mentioned measurement method, by setting the pre-treatment column before the separation columns, protein and electrolyte solution components can be automatically separated while flowing in the stream of the mobile phase. This eliminates the need of pre-treatment before introduction into the injector and as a result, decomposition of protein during measurement can be reduced to the minimum. In addition, since electrolyte solution components which co-exist in large amounts are discharged from the system by switching the 6-ways-direction switching valve, the influences of the co-existing substance is small. Further, because the molecular weight distribution of protein can also be measured in the separation column, information on the molecular weight can also be obtained, whereby the progress of decomposition of protein over the aging time can also be measured.

[0076] The temperature of the above-mentioned copper electrolyte solution upon copper electrolysis is usually 40° C. to 60° C., preferably 45° C. to 55° C. A temperature within this range is preferable because the obtained deposited foil may have uniform shape and size of mountains of the rough surface and low roughness. A temperature lower than 40° C. is not preferable because shapes of the mountains of the rough surface tend to be random, and a temperature higher than 60° C. is not preferable because it tends to accelerate deterioration of equipment such as vinyl chloride piping.

[0077] The above-mentioned copper electrolyte solution can be produced according to a known method. For example, the copper concentration can be increased by dissolving a copper raw material such as copper wire scrap in an existing copper electrolyte solution, and the free  $\text{SO}_4^{2-}$ -concentration and the  $\text{Cl}^-$  concentration can be increased by adding sulfuric acid or hydrochloric acid. The number average molecular weight  $M_n$  and the concentration of protein in the copper electrolyte solution can be adjusted, after being measured by the above-mentioned measuring method, by adding a required amount of an aqueous solution of protein of which the number average molecular weight  $M_n$  is adjusted to a required level.

(Method of Producing Electrolytic Copper Foil of the Present Invention)

[0078] Next, the method of producing an electrolytic copper foil of the present invention is described. This method produces a deposited foil using the above-mentioned copper electrolyte solution for producing an electrolytic copper foil, and as a method of producing a deposited foil, a known method may be employed. Examples of such known method of producing deposited foil include, for example, a method in which copper electrolyte solution is supplied between the curved cathode surface of a revolving drum-shaped titanium cathode and an anode to conduct electrolysis, thereby depositing in the form of a deposited foil on the surface of the cathode and continuously taking up the foil.

[0079] The temperature upon electrolysis of the copper electrolyte solution used in the present invention is usually 40° C. to 60° C., preferably 45° C. to 55° C. A temperature within this range is preferable because the obtained deposited foil may have uniform shape and size of mountains of the rough surface and low roughness. A temperature lower than 40° C. is not preferable because shapes of mountains of the rough surface tend to be random, and a temperature higher than 60° C. is not preferable because it tends to accelerate deterioration of equipment such as vinyl chloride piping.

[0080] In addition, in the present invention, the current density for electrolysis upon electrolysis of the copper electrolyte solution is usually 30 A/cm<sup>2</sup> to 70 A/cm<sup>2</sup>, preferably 40 A/cm<sup>2</sup> to 60 A/cm<sup>2</sup>. A current density for electrolysis within this range is because the obtained deposited foil may have uniform shape and size of mountains of the rough surface and low roughness. The surface of the cathode may be polished accordingly so as to set  $R_z$  to, for example, 1.2 to 1.5.

[0081] The above-mentioned copper electrolyte solution can be used as a raw material for producing a low roughness deposited foil in which the shape and the size of mountains of the rough surface are uniform. The low roughness deposited foil has a foil thickness of 35  $\mu\text{m}$  and a roughness  $R_z$  of the rough surface of usually not more than 4.2  $\mu\text{m}$ , preferably 2  $\mu\text{m}$  to 3.2  $\mu\text{m}$ , and a tensile strength in an ordinary state of usually not less than 45.0 kgf/mm<sup>2</sup>. Here,  $R_z$  means a ten point average roughness and the ordinary state means to be measured at ordinary temperatures. The method of producing an electrolytic copper foil of the present invention can be used for producing the above-mentioned deposited foil.

[0082] Hereinafter, Examples are described, but the present invention is not limited to these Examples.

#### COMPARATIVE EXAMPLE 1

[0083] As an electrolyzer for preparing a deposited foil, one with the following specification was used in which the cross-section of the channel between the anode and the cathode is rectangular and which is capable of conducting electrolysis with continuously supplying an electrolyte solution between the anode and the cathode using a circulating pump.

[0084] Amount of solution in bath: 4.5 L

[0085] Size of anode surface and cathode surface: 6 cm×11 cm

[0086] Material of anode: DSE

[0087] Material of cathode: titanium plate

[0088] Distance between anode and cathode: 5 mm

[0089] For a copper electrolyte solution, sulfuric acid, copper sulfate pentahydrate and hydrochloric acid were added to purified water and dissolved therein to prepare a solution (base solution A) of the following composition.

[0090]  $\text{Cu}^{2+}$  concentration: 82.5 g/L

[0091] free  $\text{SO}_4^{2-}$  concentration: 150 g/L

[0092]  $\text{Cl}^-$  concentration: 1.7 ppm

[0093] UDB available from Nitta Gelatin Inc. was used as gelatin, which was dissolved in pure water to prepare 1 g/L of an aqueous gelatin solution (aqueous gelatin solution A).

[0094] The aqueous gelatin solution A was added to the base solution A so that the gelatin concentration reached 1.8 ppm, followed by sufficient stirring to prepare an electrolyte solution A. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution A are shown in Table 1.

[0095] The number average molecular weight  $M_n$  and the concentration of gelatin were measured using the apparatus described in FIG. 21 under the following measurement conditions.

(Measurement Condition)

[0096] Pre-treatment column: PEEK® column 7.5 mm in inner diameter and 250 mm in length packed with Sephadex G-15 available from Amersham Pharmacia Biotech AB, which is a filler having a particle size of 66  $\mu\text{m}$  or less (molecular weight exclusion limit 1500).

Separation column: Asahipak GS-320HQ available from Showa Denko K.K. (molecular weight exclusion limit 40000, inner diameter 7.6 mm, length 300 mm)

Temperature: 25° C.

Mobile phase and flow rate: mixed solution of 20% by volume of acetonitrile and 80% by volume of diluted sulfuric acid (0.005 M), 0.6 mL/min

Injection volume: 200  $\mu\text{L}$

Method of detection: absorption of UV of 210 nm

[0097] In the measurement of the number average molecular weight  $M_n$  of gelatin, reagents used for preparing a calibration curve are as follows. The concentration of gelatin was measured by preparing a calibration curve using an aqueous solution of the same kind of gelatin of which the concentration is known.

(Reagent)

[0098] ALBUMIN, BOVINE SERUM (available from SIGMA-ALDRICH Japan K.K., molecular weight 66000)

[0099] CYTOCHROME C (available from SIGMA-ALDRICH Japan K.K. molecular weight 12400)

[0100] APROTININ (available from SIGMA-ALDRICH Japan K.K. molecular weight 6500)

[0101] INSULIN (available from SIGMA-ALDRICH Japan K.K. molecular weight 5734)

[0102] INSULIN CHAIN B, OXIDIZED (available from SIGMA-ALDRICH Japan K.K. molecular weight 3496)

[0103] NEUROTENSIN (available from SIGMA-ALDRICH Japan K.K. molecular weight 1673)

[0104] ANGIOTENSIN II (available from SIGMA-ALDRICH Japan K.K. molecular weight 1046)

[0105] VAL-GLU-GLU-ALA-GLU (available from SIGMA-ALDRICH Japan K.K. molecular weight 576)

[0106] Immediately after preparing the electrolyte solution A, electrolysis was conducted under the following conditions and a deposited foil was prepared.

[0107] Temperature of copper electrolyte solution: 52° C.

[0108] Current density for electrolysis: 50 A/cm<sup>2</sup>

[0109] Thickness of deposited foil: 35  $\mu\text{m}$

[0110] The roughness  $R_a$ ,  $R_{\text{max}}$  and  $R_z$  of rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The method of measurement is as follows. The results of the measurement are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 1.

[0111] Roughness  $R_a$ ,  $R_{\text{max}}$  and  $R_z$ : Using a contact surface roughness measuring instrument having a diamond ball tip of  $\phi$  2  $\mu\text{m}$  (available from Kosaka Laboratories Ltd., product name: SEF-30D), the surface roughness of the rough surface of the deposited foil was measured. The measurement length was 0.8 mm.  $R_a$ ,  $R_{\text{max}}$  and  $R_z$  were measured in accordance with JIS B0601, and specifically  $R_a$  represents a center line average roughness,  $R_{\text{max}}$  represents a maximum roughness and  $R_z$  represents a ten point average roughness.

[0112] Tensile strength at ordinary temperature: The obtained deposited foil was cut and a sample of width 1 cm×length 10 cm was prepared. With both ends in the longitudinal direction of the sample being each pinched with vise-like chucks provided at two positions in the vertical direction of the apparatus, the sample was set so that the longitudinal direction of the sample corresponds to the vertical direction of the apparatus, and under an ordinary temperature, the lower chuck was pulled down at a rate of 50 mm/min with the sample being pinched. The heaviest load for the measured tensile strengths was defined as a tensile strength at an ordinary temperature.

[0113] Elongation at ordinary temperature: The maximum of the measured elongations upon the measurement of the tensile strength at ordinary temperature was defined as an elongation at ordinary temperature.

#### COMPARATIVE EXAMPLE 2

[0114] After adding the aqueous gelatin solution A to the base solution A so that the gelatin concentration reached 1.8 ppm, the mixture was maintained at 50° C. for 80 hours without adding gelatin to prepare an electrolyte solution B.

The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution B are shown in Table 1.

[0115] In 80 hours from adding the aqueous gelatin solution A, electrolysis was conducted under the same conditions as in Comparative Example 1 using the electrolyte solution B to prepare a deposited foil.

[0116] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 2.

#### COMPARATIVE EXAMPLE 3

[0117] For a copper electrolyte solution, sulfuric acid, copper sulfate pentahydrate and hydrochloric acid were added to purified water and dissolved therein to prepare a solution (base solution B) of the following composition.

[0118]  $Cu^{2+}$  concentration: 84.0 g/L

[0119] free  $SO_4^{2-}$  concentration: 150 g/L

[0120]  $Cl^-$  concentration: 1.7 ppm

[0121] The aqueous gelatin solution A was added to the base solution B so that the gelatin concentration reached 2.7 ppm, followed by sufficient stirring to prepare an electrolyte solution C. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution C are shown in Table 1.

[0122] Immediately after preparing the electrolyte solution C, electrolysis was conducted under the following conditions and a deposited foil was prepared.

[0123] Temperature of copper electrolyte solution: 52° C.,

[0124] Current density for electrolysis: 50 A/cm<sup>2</sup>

[0125] Thickness of deposited foil: 35  $\mu$ m

[0126] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 3.

#### EXAMPLE 1

[0127] The aqueous gelatin solution A was added to the electrolyte solution C over a single day in an amount of 0.5 ppm each for 6 times (3 ppm in total) in terms of the concentration in the electrolyte solution. The mixture was sufficiently stirred to prepare an electrolyte solution D which is 1 day old from the initial addition of the aqueous gelatin solution A to the electrolyte solution C. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution D are shown in Table 1.

[0128] Using the electrolyte solution D, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0129] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 4.

#### EXAMPLE 2

[0130] The aqueous gelatin solution A was added to the electrolyte solution D over 1 day in an amount of 0.5 ppm each for 6 times (3 ppm in total) in terms of the concentration in the electrolyte solution. Sufficient stirring was repeated for additional 5 days to prepare an electrolyte solution E which is 6 day old from the initial addition of the aqueous gelatin solution A to the electrolyte solution C. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution E are shown in Table 1.

[0131] Using the electrolyte solution E, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0132] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 5.

#### EXAMPLE 3

[0133] The aqueous gelatin solution A was added to the electrolyte solution E over 1 day in an amount of 0.5 ppm each for 6 times (3 ppm in total) in terms of the concentration in the electrolyte solution. Sufficient stirring was repeated for additional 7 days to prepare an electrolyte solution F which is 13 day old from the initial addition of the aqueous gelatin solution A to the electrolyte solution C. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution F are shown in Table 1.

[0134] Using the electrolyte solution F, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0135] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 6.

#### COMPARATIVE EXAMPLE 4

[0136] SCP5000 available from Nitta Gelatin Inc. was used as gelatin, which was dissolved in pure water to prepare 1 g/L of an aqueous gelatin solution (aqueous gelatin solution B).

[0137] The aqueous gelatin solution B was then added to the base solution B so that the gelatin concentration reached

4.5 ppm, followed by sufficient stirring to prepare an electrolyte solution G. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution G are shown in Table 1.

[0138] Immediately after preparing the electrolyte solution G, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0139] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 7.

#### EXAMPLE 4

[0140] The aqueous gelatin solution B was added to the electrolyte solution G over 1 day in an amount of 0.5 ppm each for 6 times (3 ppm in total) in terms of the concentration in the electrolyte solution. The mixture was sufficiently stirred to prepare an electrolyte solution H which is 1 day old from the initial addition of the aqueous gelatin solution B to the electrolyte solution G. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution H are shown in Table 1.

[0141] Using the electrolyte solution H, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0142] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 8.

#### EXAMPLE 5

[0143] The aqueous gelatin solution B was added to the electrolyte solution D over 1 day in an amount of 0.5 ppm each for 6 times (3 ppm in total) in terms of the concentration in the electrolyte solution. Sufficient stirring was repeated for additional 5 days to prepare an electrolyte solution I which is 6 day old from the initial addition of the aqueous gelatin solution B to the electrolyte solution G. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution E are shown in Table 1.

[0144] Using the electrolyte solution I, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil. In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 9.

#### EXAMPLE 6

[0145] The aqueous gelatin solution B was added to the electrolyte solution E over 1 day in an amount of 0.5 ppm

each for 6 times (3 ppm in total) in terms of the concentration in the electrolyte solution. Sufficient stirring was repeated for additional 7 days to prepare an electrolyte solution J which is 13 day old from the initial addition of the aqueous gelatin solution B to the electrolyte solution G.

[0146] The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution J are shown in Table 1.

[0147] Using the electrolyte solution J, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0148] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 10.

#### COMPARATIVE EXAMPLE 5

[0149] 700F available from Nitta Gelatin Inc. was used as gelatin, which was dissolved in pure water to prepare 1 g/L of an aqueous gelatin solution (aqueous gelatin solution C).

[0150] The aqueous gelatin solution C was then added to the base solution B so that the gelatin concentration reached 1.6 ppm, followed by sufficient stirring to prepare an electrolyte solution K. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution K are shown in Table 1.

[0151] Immediately after preparing the electrolyte solution K, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0152] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 11.

#### COMPARATIVE EXAMPLE 6

[0153] After adding the aqueous gelatin solution C to the base solution B so that the gelatin concentration reached 1.6 ppm, the mixture was maintained at 52° C. for 6.5 hours without adding gelatin and an electrolyte solution L was prepared. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution L are shown in Table 1.

[0154] Using the electrolyte solution L, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0155] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The

rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 12.

#### EXAMPLE 7

[0156] The aqueous gelatin solution C was added to the electrolyte solution K over 7 hours in an amount of 0.5 ppm each for 5 times (2.5 ppm in total) in terms of the concentration in the electrolyte solution. The mixture was sufficiently stirred to prepare an electrolyte solution L which is 7 hour old from the initial addition of the aqueous gelatin solution C to the electrolyte solution K. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution L are shown in Table 1.

[0157] Using the electrolyte solution L, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0158] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 13.

#### EXAMPLE 8

[0159] The aqueous gelatin solution A was added to the base solution B in an amount of 0.5 ppm each in terms of the concentration in the electrolyte solution for 10 times per day for two days, 10 ppm thereof being added in total. The mixture was sufficiently stirred to prepare an electrolyte solution O. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution O are shown in Table 1.

[0160] Using the electrolyte solution O, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0161] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 14.

#### COMPARATIVE EXAMPLE 7

[0162] The aqueous gelatin solution B was added to the base solution B in an amount of 0.5 ppm each in terms of the concentration in the electrolyte solution for 10 times per day for two days, 10 ppm thereof being added in total. The mixture was allowed to stand for three days to prepare an electrolyte solution P. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution P are shown in Table 1.

[0163] Using the electrolyte solution P, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0164] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3.

#### EXAMPLE 9

[0165] The aqueous gelatin solution B was added to the base solution B in an amount of 0.5 ppm each in terms of the concentration in the electrolyte solution for 10 times per day for two days, 10 ppm thereof being added in total. The mixture was sufficiently stirred to prepare an electrolyte solution Q. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution Q are shown in Table 1.

[0166] Using the electrolyte solution Q, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0167] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 15.

#### COMPARATIVE EXAMPLE 8

[0168] A1576 available from Asahi Gelatine Industrial Co., Ltd was used as gelatin, which was dissolved in pure water to prepare 1 g/L of an aqueous gelatin solution (aqueous gelatin solution C). The aqueous gelatin solution C was added to the base solution B so that the gelatin concentration reached 5 ppm, followed by sufficient stirring and the mixture was allowed to stand for 5 hours to prepare an electrolyte solution R. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution R are shown in Table 1.

[0169] Using the electrolyte solution R, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0170] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 16.

#### EXAMPLE 10

[0171] The aqueous gelatin solution A was added to the base solution B in an amount of 0.5 ppm each in terms of the concentration in the electrolyte solution for 15 times per day for two days, 15 ppm thereof being added in total to prepare an electrolyte solution S. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution S are shown in Table 1.



[0172] Using the electrolyte solution S, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0173] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 17.

#### COMPARATIVE EXAMPLE 9

[0174] The aqueous gelatin solution A was added to the base solution B in an amount of 0.5 ppm each in terms of the concentration in the electrolyte solution for 15 times per day for two days, 15 ppm thereof being added in total. The mixture was allowed to stand for 80 hours as it stood to prepare an electrolyte solution T. The number average molecular weight  $M_n$  and the concentration of gelatin in the electrolyte solution T are shown in Table 1.

[0175] Using the electrolyte solution T, electrolysis was conducted under the same conditions as in Comparative Example 3 to prepare a deposited foil.

[0176] In the same manner as in Comparative Example 1, the roughness  $R_a$ ,  $R_{max}$  and  $R_z$  of the rough surface, the tensile strength in an ordinary state and the elongation in an ordinary state of the obtained deposited foil were measured. The measurement results are shown in Tables 2 and 3. The rough surface of the obtained deposited foil was photographed by a scanning electron microscope (SEM). The result is shown in FIG. 18.

TABLE 1

	Kind of base solution	Kind of aqueous gelatin solution	Kind of electrolyte solution	$M_n$ of gelatin in electrolyte solution	Concentration of gelatin in electrolyte solution (ppm)
Comparative Example 1	A	A	A	3400	1.8
Comparative Example 2	A	A	B	1400	0.6
Comparative Example 3	B	A	C	3100	2.7
Example 1	B	A	D	2000	3.0
Example 2	B	A	E	1600	2.4
Example 3	B	A	F	1300	2.2
Comparative Example 4	B	B	G	3200	4.5
Example 4	B	B	H	2000	3.0
Example 5	B	B	I	1700	2.6
Example 6	B	B	J	1400	2.4
Comparative Example 5	B	C	K	2500	1.6
Comparative Example 6	B	C	L	1700	0.8
Example 7	B	C	M	1700	2.2
Example 8	B	A	O	1300	3.0
Comparative Example 7	B	B	P	1000	0.8
Example 9	B	B	Q	1300	2.6
Comparative Example 8	B	C	R	1500	1.4
Example 10	B	A	S	1500	3.2
Comparative Example 9	B	A	T	1300	0.8

[0177]

TABLE 2

	Roughness of rough surface $R_a$ ( $\mu m$ )	Roughness of rough surface $R_{max}$ ( $\mu m$ )	Roughness of rough surface $R_z$ ( $\mu m$ )	Evaluation of mountain shape of rough surface *1	Remarks for mountains of rough surface	FIG.
Com. Ex. 1	0.80	5.2	4.7	M	Large mountains, non-uniform shapes	FIG. 1
Com. Ex. 2	1.36	9.0	7.2	M	Large mountains, non-uniform shapes	FIG. 2
Com. Ex. 3	0.77	5.8	4.8	M	Large mountains, non-uniform shapes	FIG. 3
Ex. 1	0.54	3.7	3.4	G		FIG. 4
Ex. 2	0.66	4.2	4.0	G		FIG. 5
Ex. 3	0.55	3.9	3.6	G		FIG. 6
Com. Ex. 4	0.61	4.4	4.0	G		FIG. 7
Ex. 4	0.54	5.0	3.6	G		FIG. 8
Ex. 5	0.58	3.9	3.6	G		FIG. 9
Ex. 6	0.56	4.0	3.4	G		FIG. 10

TABLE 2-continued

Com. Ex. 5	0.85	5.9	5.1	P	Peaks varying in size	FIG. 11
Com. Ex. 6	1.04	7.3	6.3	P	Peaks varying in size	FIG. 12
Ex. 7	0.47	3.5	3.0	G		FIG. 13
Ex. 8	0.35	2.7	2.4	G		FIG. 14
Com. Ex. 7	0.52	3.7	3.3	—		None

	Roughness of rough surface Ra. ( $\mu\text{m}$ )	Roughness of rough surface Rmax ( $\mu\text{m}$ )	Roughness of rough surface Rz ( $\mu\text{m}$ )	Evaluation of mountain-shape of rough surface *1	Remarks for mountains of rough surface	FIG.
Ex. 9	0.40	3.0	2.8	G		FIG. 15
Com. Ex. 8	0.67	4.9	4.3	P	Peaks varying in size	FIG. 16
Ex. 10	0.43	2.7	2.6	G		FIG. 17
Com. Ex. 9	1.0	6.9	5.4	P	Peaks varying in size	FIG. 18

\*1 G: good, M: moderate, P: poor

[0178]

TABLE 3

	Tensile strength at ordinary state ( $\text{kgf/mm}^2$ )	Elongation at ordinary state (%)
Comparative Example 1	48.6	15.9
Comparative Example 2	45.5	11.7
Comparative Example 3	49.0	18.0
Example 1	51.1	8.3
Example 2	48.4	16.0
Example 3	51.2	16.4
Comparative Example 4	49.5	15.9
Example 4	51.7	15.3
Example 5	52.8	13.4
Example 6	51.7	16.4
Comparative Example 5	48.2	13.9
Comparative Example 6	46.0	15.5
Example 7	49.5	17.2
Example 8	58.1	11.2
Comparative Example 7	—*1	—*1
Example 9	58.3	9.3
Comparative Example 8	44.7	16.6
Example 10	58.6	10.3
Comparative Example 9	55.8	9.1

\*1No data

[0179] Tables 1 to 3 show that in the case of electrolyte solutions in which the number average molecular weight  $M_n$  and the concentration of gelatin are within the predetermined ranges, the shape and the size of mountains of the rough surface of the obtained deposited foil are uniform and the obtained deposited foil has low roughness.

## INDUSTRIAL APPLICABILITY

[0180] The copper electrolyte solution for producing an electrolytic copper foil and the method of producing an electrolytic copper foil of the present invention can be used for producing an electrolytic copper foil, especially a deposited foil.

1. A copper electrolyte solution for producing an electrolytic copper foil, characterized by comprising protein having a number average molecular weight  $M_n$  of 1000 to 2300 at a concentration of 2 ppm to 4.5 ppm.

2. The copper electrolyte solution for producing an electrolytic copper foil according to claim 1, characterized in that a  $\text{Cu}^{2+}$  concentration is 60 g/L to 100 g/L.

3. The copper electrolyte solution for producing an electrolytic copper foil according to claim 1, characterized in that a free  $\text{SO}_4^{2-}$  concentration is 60 g/L to 250 g/L.

4. The copper electrolyte solution for producing an electrolytic copper foil according to claim 1, characterized in that a  $\text{Cl}^-$  concentration is 0.5 ppm to 2.0 ppm.

5. The copper electrolyte solution for producing an electrolytic copper foil according to claim 1, characterized in that the temperature is 40° C. to 60° C.

6. A method of producing an electrolytic copper foil, characterized by using the copper electrolyte solution for producing an electrolytic copper foil according to claim 1.

7. A method of producing an electrolytic copper foil, characterized by using the copper electrolyte solution for producing an electrolytic copper foil according to claim 2.

8. A method of producing an electrolytic copper foil, characterized by using the copper electrolyte solution for producing an electrolytic copper foil according to claim 3.

9. A method of producing an electrolytic copper foil, characterized by using the copper electrolyte solution for producing an electrolytic copper foil according to claim 4.

**10.** A method of producing an electrolytic copper foil, characterized by using the copper electrolyte solution for producing an electrolytic copper foil according to claim 5.

**11.** The method of producing an electrolytic copper foil according to claim 6, characterized in that the current density for electrolysis is 30 A/cm<sup>2</sup> to 70 A/cm<sup>2</sup>.

**12.** The method of producing an electrolytic copper foil according to claim 7, characterized in that the current density for electrolysis is 30 A/cm<sup>2</sup> to 70 A/cm<sup>2</sup>.

**13.** The method of producing an electrolytic copper foil according to claim 8, characterized in that the current density for electrolysis is 30 A/cm<sup>2</sup> to 70 A/cm<sup>2</sup>.

**14.** The method of producing an electrolytic copper foil according to claim 9, characterized in that the current density for electrolysis is 30 A/cm<sup>2</sup> to 70 A/cm<sup>2</sup>.

**15.** The method of producing an electrolytic copper foil according to claim 10, characterized in that the current density for electrolysis is 30 A/cm<sup>2</sup> to 70 A/cm<sup>2</sup>.

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