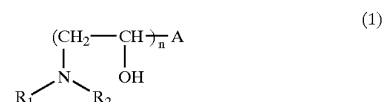




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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2004/0149583 A1**
Kumagai et al. (43) **Pub. Date: Aug. 5, 2004**(54) **COPPER ELECTROLYTE COMPRISING AMINE COMPOUND HAVING SPECIFIC SKELETON AND ORGANIC SULFUR COMPOUND AND ELECTROLYTIC COPPER FOIL PREPARED USING THE SAME**(76) Inventors: **Masashi Kumagai**, Ibaraki (JP); **Mikio Hanafusa**, Ibaraki (JP)Correspondence Address:
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Kalamazoo, MI 49008-1699 (US)(21) Appl. No.: **10/479,896**(22) PCT Filed: **May 21, 2003**(86) PCT No.: **PCT/JP03/06363**(30) **Foreign Application Priority Data**Jul. 23, 2002 (JP) 2002-213889
Oct. 3, 2002 (JP) 2002-291403**Publication Classification**(51) **Int. Cl.⁷** **C25D 1/04; C25D 3/38**
(52) **U.S. Cl.** **205/76; 205/298**(57) **ABSTRACT**

The invention has an object to obtain a low-profile electrolytic copper foil made by electrolytic copper foil manufacturing using a cathode drum such that the surface roughness on the rough surface side (the opposite side to the lustrous surface) is low. And in particular, the invention has an object to obtain an electrolytic copper foil that can be finely patterned and has excellent elongation and tensile strength at normal and high temperatures. This object is attained by using a copper electrolytic solution containing, as additives, an organosulfur compound, and an amine compound having a specific skeleton represented by undermentioned general formula (1) obtained by additively reacting an amine compound and a compound having one or more epoxy groups in a molecule thereof to an addition reaction.



(In general formula (1), R₁ and R₂ are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups, A represents an epoxy compound residue, and n represents an integer greater than or equal to 1.)

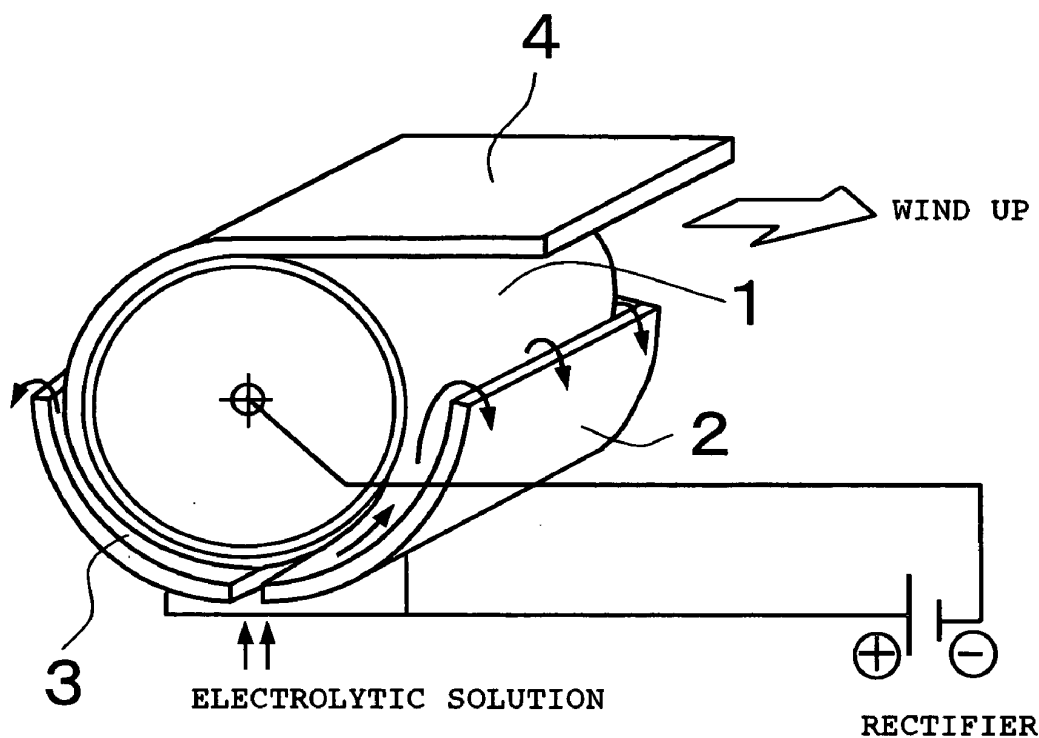


FIG. 1

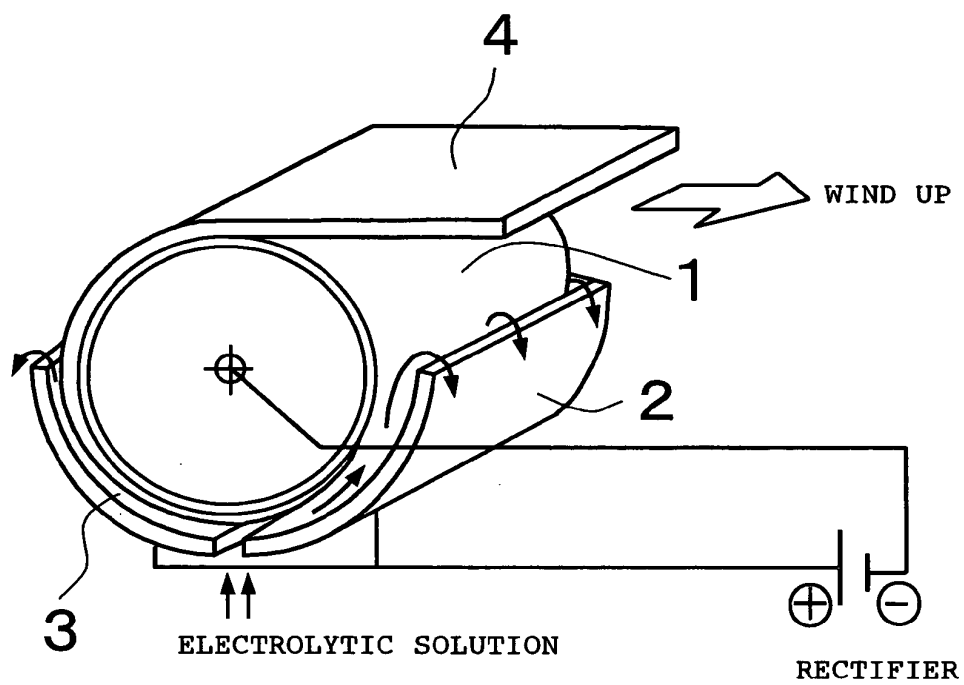


FIG. 2

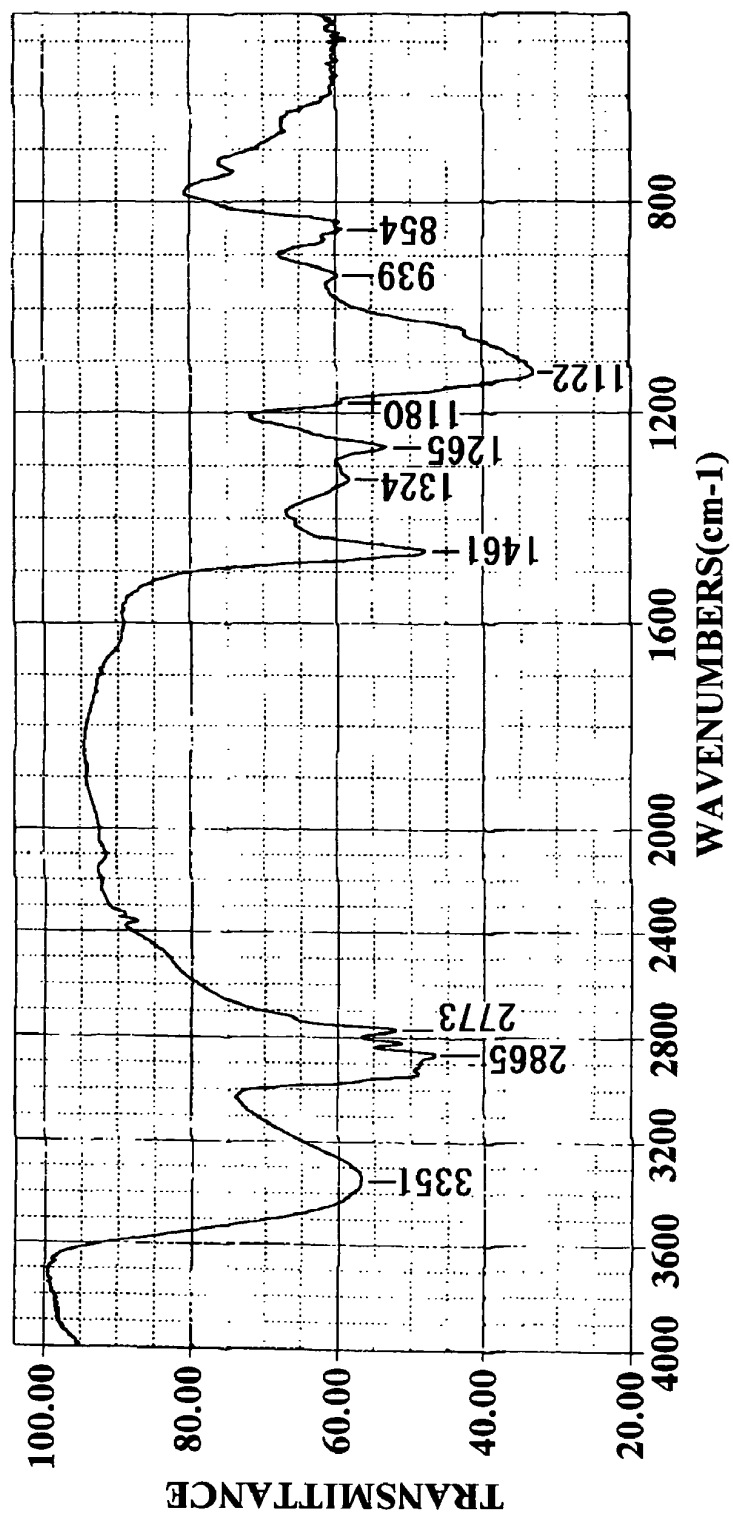


FIG. 3

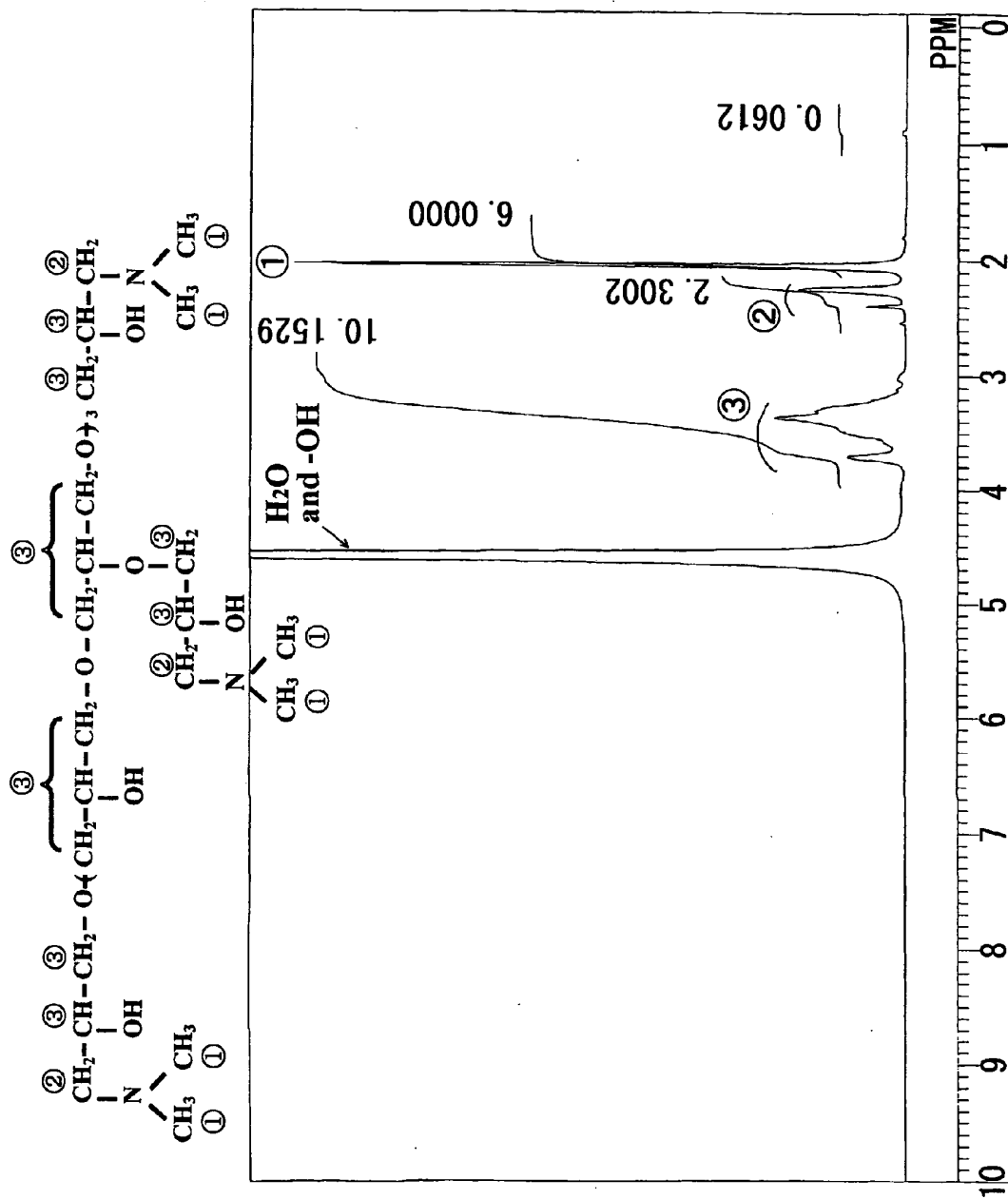
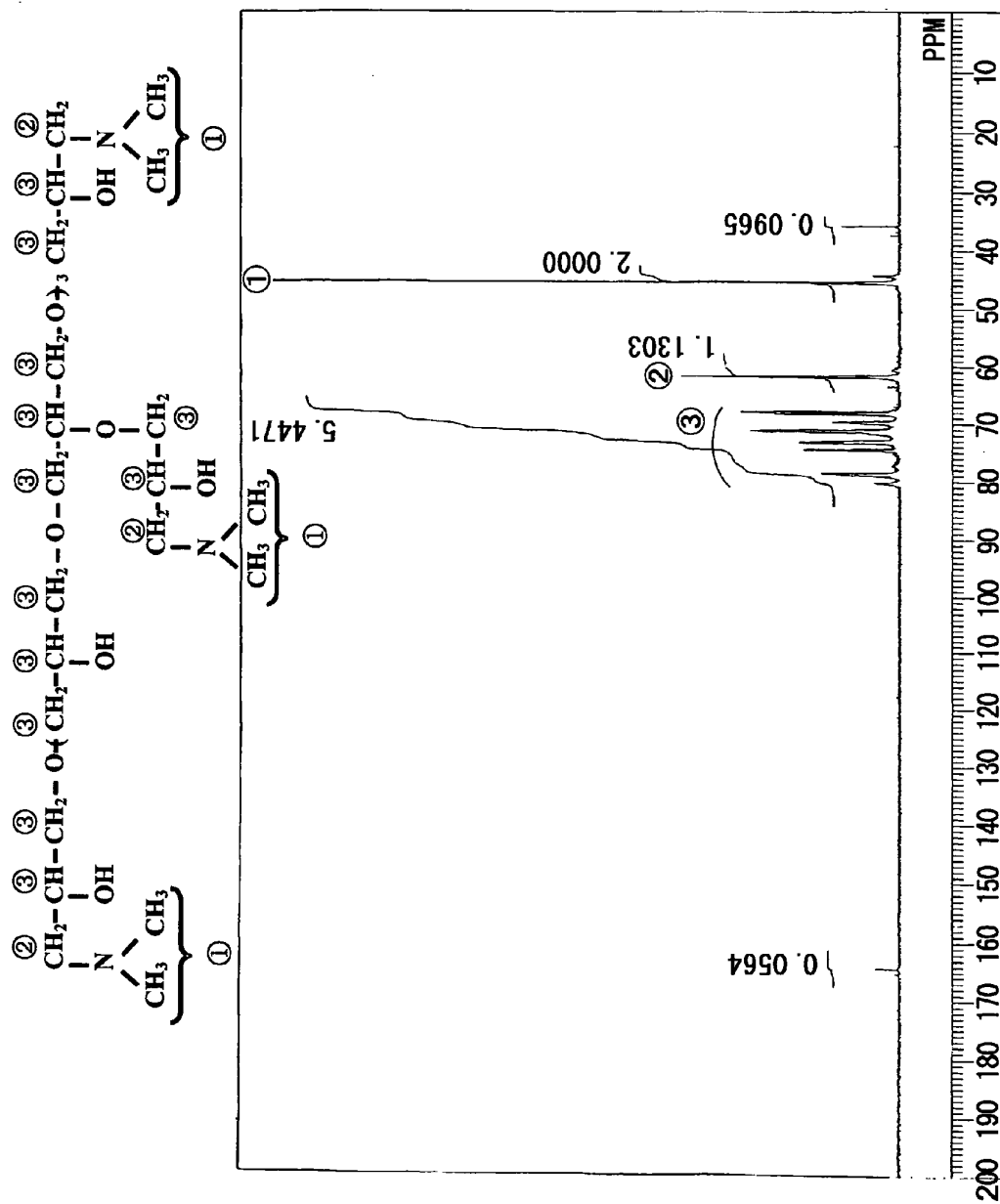


FIG. 4



**COPPER ELECTROLYTE COMPRISING AMINE
COMPOUND HAVING SPECIFIC SKELETON AND
ORGANIC SULFUR COMPOUND AND
ELECTROLYTIC COPPER FOIL PREPARED
USING THE SAME**

TECHNICAL FIELD

[0001] The present invention relates to a copper electrolytic solution used in the manufacture of an electrolytic copper foil, and in particular to a copper electrolytic solution used in the manufacture of an electrolytic copper foil that can be finely patterned and has excellent elongation and tensile strength at normal temperature and high temperature.

BACKGROUND ART

[0002] In general, to manufacture an electrolytic copper foil, a rotating metal cathode drum having a polished surface, and an insoluble metal anode that goes around the periphery of approximately the lower half of the cathode drum are used, and a copper electrolytic solution is made to flow between the cathode drum and the anode. A potential is also applied between the cathode drum and the anode, whereby copper is electrodeposited onto the cathode drum. Once the electrodeposited copper has reached a prescribed thickness, the electrodeposited copper is peeled off from the cathode drum, whereby copper foil is manufactured continuously.

[0003] Copper foil obtained in this way is generally referred to as raw foil; this raw foil is subsequently subjected to various surface treatment and is then used in printed wiring boards or the like.

[0004] A conventional copper foil manufacturing apparatus is shown schematically in **FIG. 1**. In this electrolytic copper foil apparatus, a cathode drum is installed in an electrolysis bath housing an electrolytic solution. The cathode drum **1** rotates in a state partially submerged (i.e. with approximately the lower half submerged) in the electrolytic solution.

[0005] An insoluble anode **2** is provided so as to go around the lower half of the outer periphery of the cathode drum **1**. There is a constant gap **3** between the cathode drum **1** and the anode **2**, and the electrolytic solution flows through this gap. In the apparatus of **FIG. 1**, two anode plates are used.

[0006] In **FIG. 1**, the constitution is such that the electrolytic solution is fed in from below, passes through the gap **3** between the cathode drum **1** and the anode **2**, and flows over upper edges of the anode **2**, thus circulating. A prescribed voltage is maintained between the cathode drum **1** and the anode **2** using a rectifier.

[0007] As the cathode drum **1** rotates, the copper electrodeposited from the electrolytic solution grows thicker, and once the copper has become at least a certain thickness, the raw foil **4** is peeled off, and is wound up continuously. The thickness of the raw foil manufactured in this way is adjusted through the distance between the cathode drum **1** and the anode **2**, the flow rate of the electrolytic solution fed in, and the amount of electricity fed in.

[0008] With copper foil manufactured using such an electrolytic copper foil manufacturing apparatus, the surface contacting the cathode drum becomes a specular surface, but

the surface on the other side becomes a rough surface having irregularities. With ordinary electrolysis, the irregularities on the rough surface are severe, and hence there is a problem that undercutting is prone to occurring during etching, and thus fine patterning is difficult.

[0009] However, recently, as the density on printed wiring boards has been increased, the circuit width has been reduced and the number of layers has been increased, and accompanying this copper foil that can be finely patterned has come to be required. To carry out fine patterning, copper foil having crystal grains of a uniform size and having a uniform etching rate and a uniform solubility, i.e. copper foil having excellent etching properties, is required.

[0010] Moreover, regarding properties required of copper foil for printed wiring boards, not only elongation at normal temperature, but also elongation at high temperature are required to prevent cracking due to thermal stress. Furthermore, high tensile strength for dimensional stability of printed wiring boards are required. However, copper foil for which irregularities on the rough surface are severe as above causes a problem of not being suited to fine patterning at all as described above. Studies have thus been proceeded into making the rough surface have a low profile.

[0011] It is known that, in general, a low profile can be achieved by adding a large amount of animal glue or thiourea to the electrolytic solution. However, such additives have a problem of causing the elongation percentage to drop dramatically at normal temperature and high temperature, thus causing a great deterioration in the properties as a copper foil for printed wiring boards.

DISCLOSURE OF THE INVENTION

[0012] It is an object of the present invention to obtain a low-profile electrolytic copper foil by electrolytic copper foil manufacturing using a cathode drum such that the surface roughness on the rough surface side (the opposite side to the lustrous surface) is low. And in particular, it is an object to obtain an electrolytic copper foil that can be finely patterned and has excellent elongation and tensile strength at normal temperature and high temperature.

[0013] The present inventors found that by adding optimum additives enabling a low profiled foil to an electrolytic solution, therefore, it is possible to obtain an electrolytic copper foil that can be finely patterned and has excellent elongation and tensile strength at normal temperature and high temperature.

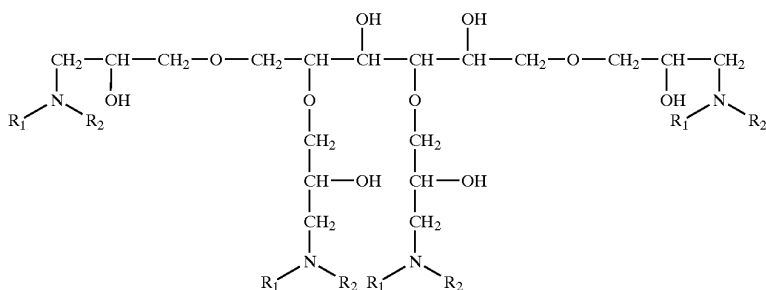
[0014] Based on this finding, the present inventors discovered that, by electrolysis using a copper electrolytic solution containing an amine compound having a specific skeleton and an organosulfur compound, it is possible to obtain an electrolytic copper foil that can be finely patterned and has excellent elongation and tensile strength at normal temperature and high temperature, in the case of an electrolytic copper foil manufacturing method in which a copper electrolytic solution is made to flow between a cathode drum and an anode, copper is electrodeposited onto the cathode drum, and the electrodeposited copper is peeled off from the cathode drum to continuously manufacture copper foil; the present invention was thus achieved.

[0015] Specifically, the present invention is constituted as follows.

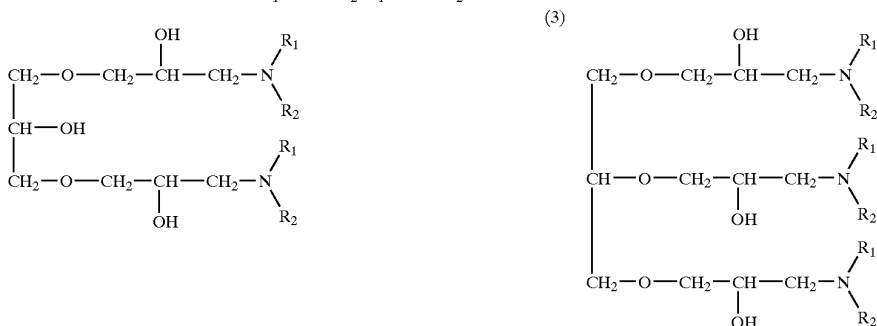
[0016] (1) A copper electrolytic solution containing, as additives, an organosulfur compound, and an amine compound having a specific skeleton represented by undermentioned general formula (1) obtained by additively reacting an amine compound and a compound having one or more epoxy groups in a molecule thereof.

[0018] (2) A copper electrolytic solution according to (1) above, wherein the epoxy compound residue A of said amine compound having a specific skeleton has a linear ether linkage.

[0019] (3) A copper electrolytic solution according to (1) or (2) above, wherein said amine compound having a specific skeleton includes any of undermentioned general formulae (2) to (9).

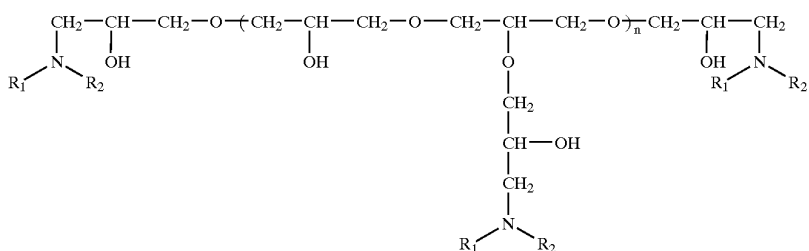


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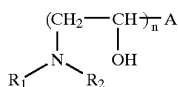
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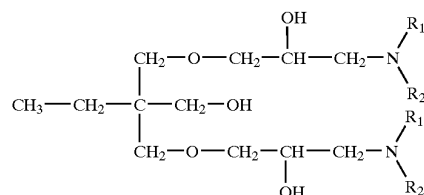
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[0020] (n: an integer from 1 to 5)

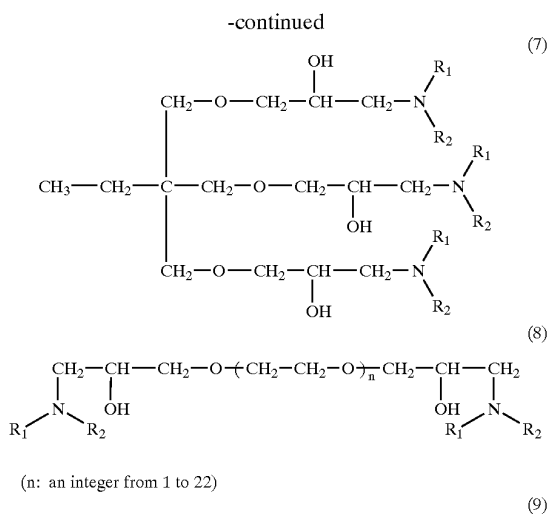


(1)

[0017] (In general formula (1), R₁ and R₂ are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups, A represents an epoxy compound residue, and n represents an integer greater than or equal to 1.)



(6)



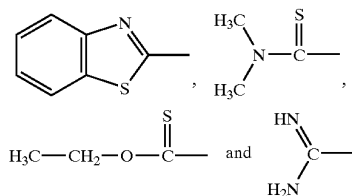
[0021] (n: an integer from 1 to 3)

[0022] (In general formulae (2) to (9), R₁ and R₂ are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups.)

[0023] (4) A copper electrolytic solution according to (1) above, wherein said organosulfur compound is a compound represented by undermentioned general formula (10) or (11).



[0024] (In general formulae (10) and (11), R¹, R² and R³ are each an alkylene group having 1 to 8 carbon atoms, R⁴ is selected from a group consisting of hydrogen,



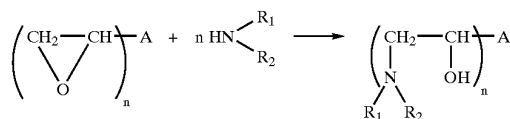
[0025] , X is selected from a group consisting of hydrogen, a sulfonic acid group, a phosphonic acid group, and sulfonic acid or phosphonic acid alkali metal salt groups or ammonium salt groups, Y is sulfur or phosphorus, Z¹ and Z² are each hydrogen, sodium or potassium, and n is 2 or 3.)

[0026] (5) An electrolytic copper foil produced using the copper electrolytic solution according to any of (1) through (4) above.

[0027] (6) A copper-clad laminate using the electrolytic copper foil according to (5) above.

[0028] In the present invention, it is important for the electrolytic solution to contain an organosulfur compound, and the amine compound having the specific skeleton represented by above-mentioned general formula (1) that is obtained through an addition reaction between an amine compound and a compound having one or more epoxy groups in a molecule thereof. If only one of these were to be added, then it would not be possible to attain the object of the present invention.

[0029] The amine compound (1) having the specific skeleton is synthesized through the addition reaction represented by the undermentioned reaction formula. Specifically, the amine compound having the specific skeleton can be produced by mixing together an amine compound and a compound having one or more epoxy groups in a molecule thereof, and reacting for approximately 30 minutes to 6 hours at 50 to 150° C.

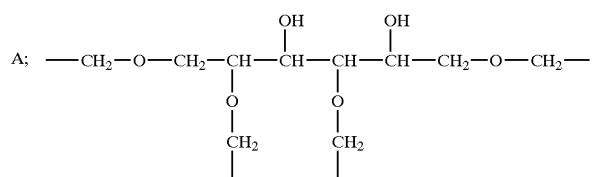
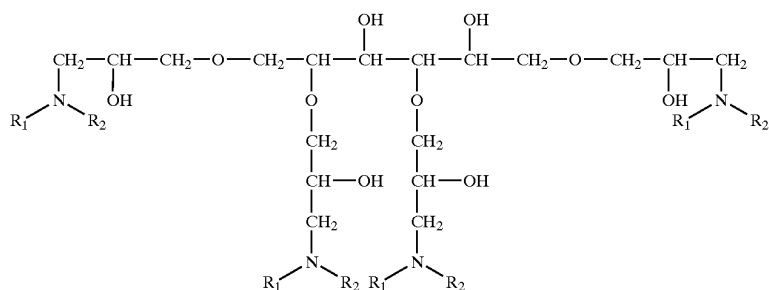


[0030] (In the above formula, R₁ and R₂ are each selected from the set consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups, A represents an epoxy residue, and n represents an integer greater than or equal to 1.)

[0031] Specific examples of R₁ and R₂ in the structure of the amine compound having the specific skeleton are a hydroxyethyl group and a hydroxyisopropyl group ('hydroxyalkyl groups' above), a 2-ethoxyethyl group and a 2-propoxyethyl group ('ether groups' above), a phenyl group and a naphthyl group ('aromatic groups' above), a tolyl group, a xylyl group, a cumenyl group and a 1-phenylethyl group ('aromatic-substituted alkyl groups' above), an allyl group, a 1-propenyl group, an isopropenyl group, a 1-butenyl group, a 2-butenyl group and a 2-methylallyl group ('unsaturated hydrocarbon groups' above), and a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group and an octyl group ('alkyl groups' above). From the viewpoint of water-solubility, substituents having too large a number of carbon atoms are not desirable, with it being preferable for the number of carbon atoms per one substituent to be not more than 8.

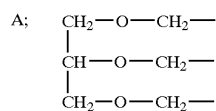
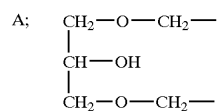
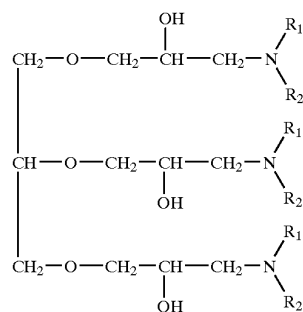
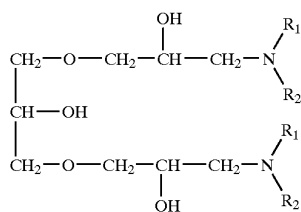
[0032] It is preferable for the amine compound having the specific skeleton to be a compound having a linear ether linkage in the epoxy compound residue A. Compounds having the structural formulae of undermentioned general formulae (2) to (9) are preferable as such compounds in which the epoxy compound residue A has a linear ether linkage, with the epoxy compound residue A in each of general formulae (2) to (9) being as shown below.

(2)

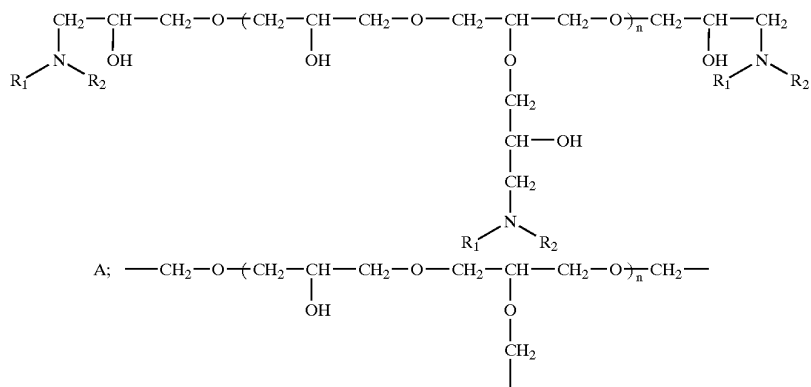


(3)

(4)



(5)



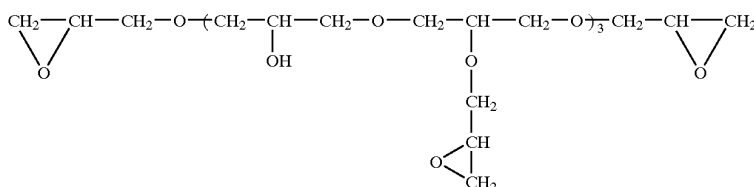
[0033] (n: an integer from 1 to 5)

BEST MODE FOR CARRYING OUT THE INVENTION

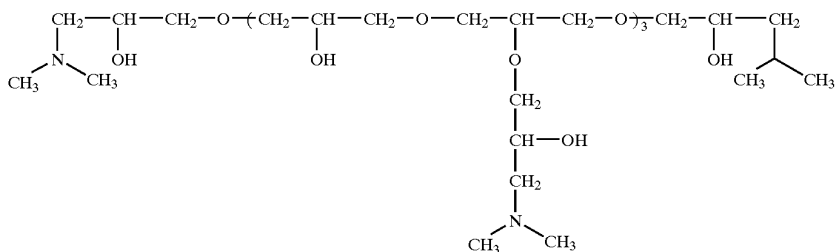
[0048] Following is a more detailed description of the present invention, showing examples.

Example of Synthesis of the Amine Compound Having the Specific Skeleton

[0049] 10.0 g of the epoxy compound represented by the undermentioned chemical formula (Denacol EX-521 made by Nagase Kasei Kogyo K.K.) (0.0544 mol of epoxy groups) and 10.7 g (0.0544 mol) of dibenzylamine were put into a 3-mouth flask, and using a condenser tube with dry ice-methanol as a coolant, reaction was carried out at 60° C. for 3 hours, thus obtaining an epoxy resin modified with dibenzylamine.



[0050] Similarly, epoxy resins modified with each of bis(2-ethoxyethyl)amine, diethanolamine, diphenylamine, diallylamine and dimethylamine were obtained. The FT-IR, ¹H-NMR and ¹³C-NMR spectra of the epoxy resin modified with dimethylamine are shown in FIGS. 2 to 4. The compound obtained was the dimethylamine compound represented by the undermentioned chemical formula.



EXAMPLES 1 TO 12 AND COMPARATIVE
EXAMPLES 1 TO 9

[0051] 35 μm electrolytic copper foil was manufactured using an electrolytic copper foil manufacturing apparatus as shown in **FIG. 1**. The composition of the electrolytic solu-

tion was as follows, with the amounts added of the additives being as shown in Table 1.

Cu:	90 g/l
H ₂ SO ₄ :	80 g/l
Cl:	60 ppm
Temperature:	55 to 57° C.
Additive A:	Disodium bis(3-sulfopropyl)disulfide (CPS, made by Raschig Inc.)
Additive B:	Sodium 3-mercapto-1-propanesulfonate (MPS, made by Raschig Inc.)
Additive C:	The amine compound having the specific skeleton obtained in the example of synthesis described above
C1:	Dibenzylamine-modified substance
C2:	Bis(2-ethoxyethyl)amine-modified substance
C3:	Diethanolamine-modified substance
C4:	Diphenylamine-modified substance

-continued

C5:	Diallylamine-modified substance
C6:	Dimethylamine-modified substance

[0052] The surface roughness Rz (μm) of each electrolytic copper foil obtained was measured in accordance with JIS B

0601, and the normal-temperature elongation (%), the normal-temperature tensile strength (kgf/mm²), the high-temperature elongation (%) and the high-temperature tensile strength (kgf/mm²) were measured in accordance with IPC-TM650. The results are shown in Table 1.

TABLE 1

	Additive A (ppm)	Additive B (ppm)	Additive C (ppm)						Rz (μ m)	Elongation*1 (%)	Tensile strength*1 (kgf/mm ²)	Elongation*2 (%)	Tensile strength*2 (kgf/mm ²)
			C1	C2	C3	C4	C5	C6					
Example 1	50	0	50	0	0	0	0	0	1.02	8.10	32.2	13.9	21.7
Example 2	50	0	0	50	0	0	0	0	1.00	6.62	30.5	16.2	21.0
Example 3	50	0	0	0	50	0	0	0	0.90	8.71	31.0	18.2	20.6
Example 4	50	0	0	0	0	50	0	0	1.13	8.90	37.9	12.6	20.7
Example 5	50	0	0	0	0	0	50	0	1.15	7.12	34.2	12.1	20.1
Example 6	50	00	0	0	0	0	0	50	0.97	6.75	31.5	16.9	21.1
Example 7	0	50	50	0	0	0	0	0	1.10	8.23	32.9	14.2	20.8
Example 8	0	50	0	50	0	0	0	0	1.02	6.69	31.2	17.0	22.3
Example 9	0	50	0	0	50	0	0	0	0.92	8.90	33.0	17.3	22.2
Example 10	0	50	0	0	0	50	0	0	1.16	8.70	36.6	12.3	21.0
Example 11	0	50	0	0	0	0	50	0	1.20	7.23	34.9	12.4	20.3
Example 12	0	50	0	0	0	0	0	50	0.98	6.83	31.9	16.5	21.4
Comparative Example 1	0	0	0	0	0	0	0	0	5.8	8.90	37.9	12.6	20.7
Comparative Example 2	100	0	0	0	0	0	0	0	5.3	0.2	10.3	1.0	15.3
Comparative Example 3	0	100	0	0	0	0	0	0	6.1	0.2	11.2	1.2	14.9
Comparative Example 4	0	0	100	0	0	0	0	0	5.3	0.3	10.9	1.1	16.0
Comparative Example 5	0	0	0	100	0	0	0	0	5.8	0.1	11.1	1.0	15.8
Comparative Example 6	0	0	0	0	100	0	0	0	5.3	0.2	12.3	1.3	15.3
Comparative Example 7	0	0	0	0	0	100	0	0	5.8	0.2	13.0	1.2	14.9
Comparative Example 8	0	0	0	0	0	0	100	0	5.2	0.2	12.2	1.1	15.9
Comparative Example 9	0	0	0	0	0	0	0	100	4.9	0.2	10.3	2.7	12.8

*1 at normal temperature

*2 at high temperature

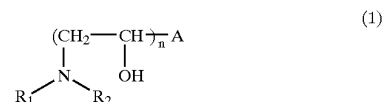
[0053] As shown in Table 1 above, for Examples 1 to 12 in which the additives of the present invention (the amine compound having the specific skeleton and the organosulfur compound) were added, each Rz was in a range of 0.90 to 1.20 μ m, each normal-temperature elongation was in a range of 6.62 to 8.90%, each normal-temperature tensile strength was in a range of 30.5 to 37.9 kgf/mm², each high-temperature elongation was in a range of 12.1 to 18.2%, and each high-temperature tensile strength was in a range of 20.1 to 22.3 kgf/mm². In this way, even though a remarkably low profile was achieved, the normal-temperature elongation, the normal-temperature tensile strength, the high-temperature elongation and the high-temperature tensile strength all exhibited values similar to or better than those of Comparative Example 1 in which no additives were added. In contrast, for Comparative Example 1 in which no additives were added and Comparative Examples 2 to 9 in which only one of the additives was added, a low profile was not achieved. Moreover, in the cases in which only one of the additives was added, the normal-temperature elongation, the normal-temperature tensile strength, the high-temperature elongation and the high-temperature tensile strength actually became worse.

[0054] Industrial Applicability

[0055] As described above, the copper electrolytic solution of the present invention to which the amine compound having the specific skeleton and the organosulfur compound have been added is extremely effective in making the rough

surface of an electrolytic copper foil obtained have a low profile; moreover excellent properties are observed in that extension properties can be maintained effectively not only at normal temperature but also at high temperature, and furthermore high tensile strength can similarly be obtained. Moreover, it is understood that addition of both the amine compound having the specific skeleton and the organosulfur compound is important, since only then can the above properties be obtained.

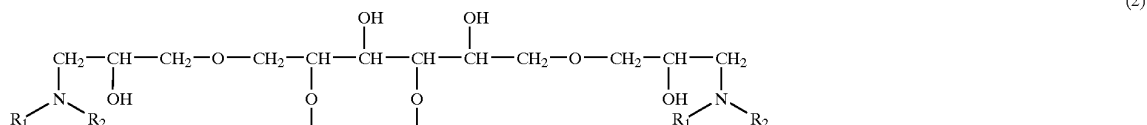
1. A copper electrolytic solution containing, as additives, an organosulfur compound, and an amine compound having a specific skeleton represented by undermentioned general formula (1) obtained by additively reacting an amine compound and a compound having one or more epoxy groups in a molecule thereof.



(In general formula (1), R₁ and R₂ are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups, A represents an epoxy compound residue, and n represents an integer greater than or equal to 1.)

2. A copper electrolytic solution according to claim 1, wherein the epoxy compound residue A of said amine compound having a specific skeleton has a linear ether linkage.

3. A copper electrolytic solution according to claim 1 or 2, wherein said amine compound having a specific skeleton includes any of undermentioned general formulae (2) to (9).

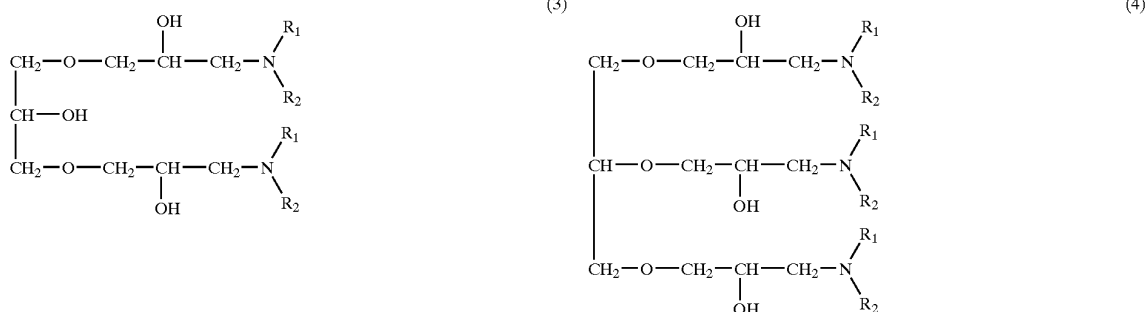


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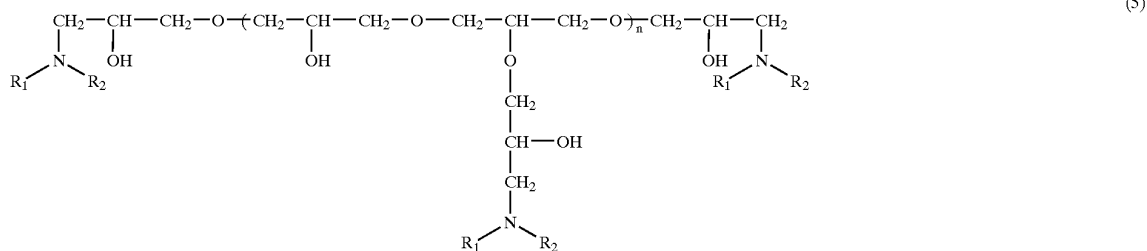


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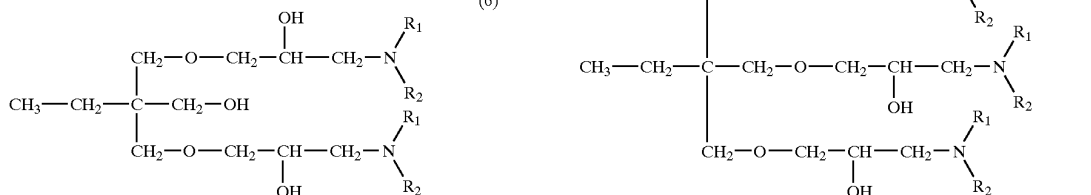


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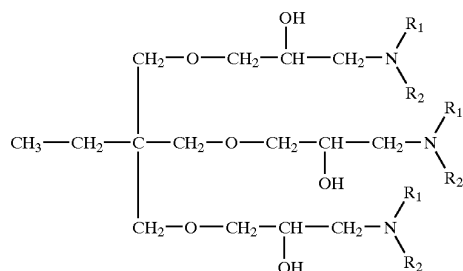
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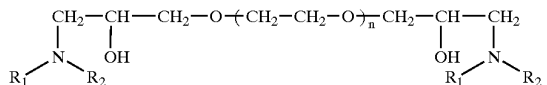


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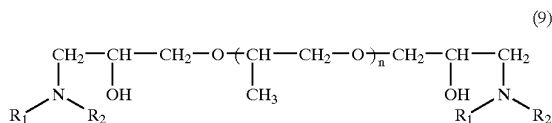
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(n: an integer from 1 to 22)



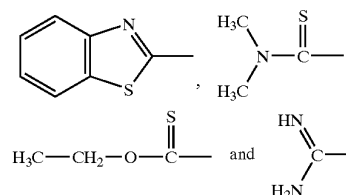
(n: an integer from 1 to 3)

(In general formulae (2) to (9), R_1 and R_2 are each selected from a group consisting of hydroxyalkyl groups, ether groups, aromatic groups, aromatic-substituted alkyl groups, unsaturated hydrocarbon groups, and alkyl groups.)

4. A copper electrolytic solution according to claim 1, wherein said organosulfur compound is a compound represented by undermentioned general formula (10) or (11).



(In general formulae (10) and (11), R^1 , R^2 and R^3 are each an alkylene group having 1 to 8 carbon atoms, R^4 is selected from a group consisting of hydrogen,



, X is selected from a group consisting of hydrogen, a sulfonic acid group, a phosphonic acid group, and sulfonic acid or phosphonic acid alkali metal salt groups or ammonium salt groups, Y is sulfur or phosphorus, Z^1 and Z^2 are each hydrogen, sodium or potassium, and n is 2 or 3.)

5. An electrolytic copper foil produced using the copper electrolytic solution according to any of claims 1 through 4.

6. A copper-clad laminate using the electrolytic copper foil according to claim 5.

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