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(54) Additives for accelerator solution for electroless metal plating

(57) Additives for accelerator solutions are provided which contain one or more accelerator solution suspension inhibiting compounds. By using accelerator solutions containing such additives in accelerator treatment processes for electroless copper plating methods, an increase in the turbidity of the accelerator solution can be prevented.

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Description

Background of the Invention

[0001] The present invention relates to accelerator solution additives and accelerator solutions for electroless metal plating. In particular, the present invention relates to an electroless copper plating method that employs such accelerator solution, and a composite material manufactured by such method.

[0002] In general, the pretreatment process for electroless copper plating consists of processes that include a conditioning process, etching process, acid wash process, palladium tin catalyst attachment process and an accelerator treatment process. In the catalyst affixing process, palladium-tin colloid is adsorbed on a substrate surface, and by washing this material with water, the affixed colloid is hydrolyzed, and part of the tin forms a Sn(OH)Cl deposit. The rest of the tin is present as tetravalent tin, and the palladium is present as a palladium salt. In the accelerator treatment process, treatment of the substrate is carried out using an acid such as hydrochloric acid, sulfuric acid or fluoroboric acid as accelerator, thereby causing dissolution of the tin salt that had formed the deposit. In addition, metallic palladium is produced by means of an acid reduction reaction with the palladium salt that had previously been removed from its colloidal state. The metallic palladium on the substrate thus functions as activated catalyst nuclei for metallic copper deposition during electroless copper plating.

[0003] When using a conventional accelerator solution having hydrochloric acid, sulfuric acid or fluoroboric acid as a primary component of the accelerator treatment solution, the turbidity of the accelerator solution increases over the course of intermittent use. An explanation that provides comprehensive understanding of the cause of this phenomenon cannot be offered, but one possibility is that the tin of the palladium tin catalyst affixed to the substrate is released into the accelerator solution, and the elemental tin is then converted into an insoluble compound. It is known empirically that this increase in turbidity in the accelerator solution is one of the causes of roughening of the copper layer in copper-resin composite materials obtained by means of electroless copper plating treatments. Roughening of the copper layer is particularly dramatic when the electroless copper plating treatment has poor leveling capacity.

[0004] The increase in turbidity of the accelerator solution as described above, in some cases, occurs to the extent that the solution cannot be used after just one day of use during of normal pretreatment processes. In comparison to solutions that are used in other pretreatment processes, frequent exchange of the accelerator solution is necessary, which is problematic in terms of industrial efficiency and running costs. An increase in the life of accelerator solutions is thus desired.

Summary of the Invention

[0005] The present invention was developed in light of this state of affairs, and has the objective of offering additive containing accelerator solution suspension-inhibiting compounds having certain structures, which control the turbidity of accelerator solutions used in the above described activation processes. An additional objective is to offer an accelerator solution containing the aforementioned accelerator solution suspension-inhibiting compounds, which controls the turbidity when used.

[0006] In addition, the present invention offers an electroless copper plating method that employs an accelerator solution containing the aforementioned accelerator solution suspension-inhibiting compounds. The invention also offers a composite material having a copper thin film produced by such method.

[0007] The present invention provides additives for accelerator solutions, such solutions comprising one or more accelerator solution suspension-inhibiting compounds having certain structures. In addition, the present invention offers an electroless copper plating method that employs an accelerator solution containing one or more of the aforementioned accelerator solution suspension-inhibiting compounds and a composite material produced by said method.

Detailed Description of the Invention

[0008] Examples of the accelerator solution suspension-inhibiting compounds of the present invention include, but are not limited to, cysteine, cystine, thiomalic acid, methionine, thiodisuccinic acid, oxalic acid, hydroxyacetic acid, glyoxylic acid, lactic acid, itaconic acid, 2-pyrrolidone-5-carboxylic acid, ascorbic acid, hydroquinone, aminopyrazine, 3-amino-1H-1,2,4-triazole, thiourea, urea, adenine, guanidine, allantoin, 2-amino-5-methyl-1,3,4-thiadiazole, hydroxylamine, cystamine, hydrazine, 1-(2,3-dihydroxypropyl)benzotriazole, 2-imidazolidinone, o-toluidine-4-sulfonic acid, 1,3-phenylenediamine-4-sulfonic acid, sulfosalicylic acid, phenolsulfonic acid, phosphoric acid, phosphonic acid, hydroxyethylidene diphosphonic acid, boric acid, tetraboric acid and salts of these compounds.

[0009] Preferable examples of such accelerator solution suspension-inhibiting compounds are cysteine, cystine, thiomalic acid, methionine, thiodisuccinic acid, oxalic acid, hydroxyacetic acid, glyoxylic acid, lactic acid, itaconic acid, 2-pyrrolidone-5-carboxylic acid, ascorbic acid, hydroquinone, aminopyrazine, 3-amino-1H-1,2,4-triazole, thiourea,

urea, adenine, hydroxyethylidene diphosphonic acid and salts of these compounds. More preferably, such compounds are cysteine, cystine, thiomalic acid, methionine, thiodisuccinic acid, ascorbic acid and slats of these compounds, still more preferably cysteine, cystine, thiomalic acid and salts of these compounds, and most preferably thiomalic acid and salts thereof.

[0010] The salts of the accelerator solution suspension-inhibiting compounds presented above may be any salt that is water soluble and can be formed by the respective compounds. When the compound has carboxylic acid groups, sulfonic acid groups, phosphoric acid groups, phosphonic acid groups and/or boric acid groups, any substance that does not impede the objectives of the present invention can be used as the substances for forming salts with these groups are. Examples of salts that are formed include, but are not restricted to, alkali metal salts, alkaline earth metal salts and ammonium salts. In addition, when the compound has primary, secondary or tertiary amine structures, these amines can form quaternary ammonium structures, and configurations may also be used that involve salts formed from said ammonium structures and acid. In addition, with hydrazine, configurations may be used that involve salts formed from hydrazinium compound and acid. Examples of acids that form salts include any acid that does not impede the objectives of the present invention, examples of which include, but are not limited to, hydrochloric acid, sulfuric acid, phosphoric acid and nitric acid. The term "water soluble" used herein applies to any compound that has a degree of water solubility that allows dissolution in the accelerator solution.

[0011] The accelerator solution additive pertaining to the present invention comprises one or more of the aforementioned accelerator solution suspension-inhibiting compounds. An increase in turbidity of the accelerator solution can be reduced or eliminated by the addition of the additive to the accelerator solution.

[0012] While not intended to be bound by theory, the increase in accelerator solution turbidity is thought to occur when the tin released from the substrate upon immersion of the substrate with affixed palladium tin catalyst in the accelerator solution is converted into a compound that is insoluble in the accelerator solution, thus forming a sediment and increasing the turbidity of the accelerator solution. In addition, although a theoretical understanding should not be expected, the mechanism whereby the increase in turbidity of the accelerator solution is controlled by the aforementioned accelerator solution suspension-inhibiting compound of the present invention is thought to involve the formation of a chelate between the accelerator solution suspension-inhibiting compound and tin ions in the accelerator solution, thereby preventing conversion of the tin into an insoluble compound.

[0013] The accelerator solution additives of the present invention can also optionally contain acid other than the aforementioned accelerator solution suspension-inhibiting compound. The acid can be any acid, provided that it is an acid other than the accelerator solution suspension-inhibiting compound. Suitable examples include, but are not restricted to, hydrochloric acid, sulfuric acid, fluoroboric acid and alkylsulfonic acid. In addition, mixtures of two or more of the acids can be contained therein. Typically, the other acid is any acid that is commonly used in other accelerator treatment processes. It is preferable for the acid other than the accelerator solution suspension-inhibiting compound to be an alkylsulfonic acid, with methanesulfonic acid being particularly desirable.

[0014] When the additive for accelerator solutions of the present invention contains acid other than the accelerator solution suspension-inhibiting compounds, the ratio of the amount of the accelerator solution suspension-inhibiting compound to such other acid can be easily determined. However, when added to the accelerator solution, it is preferred that the amount of accelerator solution suspension-inhibiting compound is an amount that allows the accelerator solution suspension-inhibiting compound to manifest superior prevention effects. It is also preferable for the amount of the other acid to be the amount that is required for the accelerator treatment.

[0015] In addition, the present additive for accelerator solutions can also contain one or more nonionic surfactants. The nonionic surfactant can be of any type, provided that it does not interfere with the objectives of the present invention. Examples of nonionic surfactants include, but are not limited to, polyethylene glycol, polyoxyethylene alkylphenol, polyoxyethylene styrenated phenol, polyoxypropylene-polyoxyethylene polymer and glycerin.

[0016] If the present additives for accelerator solutions comprise accelerator solution suspension-inhibiting compound and one or more other acids and/or nonionic surfactant, then the additive can be constituted by these components alone, or can further comprise an appropriate solvent such as water.

[0017] The accelerator solution of the present invention is preferably an aqueous solution that contains one or more accelerator solution suspension-inhibiting compounds and one or more other acids. The amount of accelerator solution suspension-inhibiting compound contained in the present accelerator solution is determined appropriately based on the conditions of use of the accelerator solution, and the type of accelerator solution suspension-inhibiting compound used therein. However, the amount is generally in the range of 0.001-50 g/L, with 0.005-10 g/L being preferred. The amount of the other acid is an amount that is commonly used in accelerator treatment processes, and is generally 25-100 g/L, with 40-60 g/L being preferred.

[0018] As described above, the accelerator solution of the present invention can contain nonionic surfactant. The amount of nonionic surfactant is generally 0.001-20 g/L, with 0.01-15 g/L being preferred.

[0019] The accelerator solution of the present invention can be used in any electroless copper plating method, provided that the method has an acceleration process whereby a palladium tin catalyst is activated. When the accelerator

solution of the present invention is used in electroless copper plating methods for accelerator treatment processes in which palladium tin catalyst is activated, it is possible to control any increase in turbidity that accompanies the use of such accelerator solutions.

[0020] The present accelerator treatment process is carried out by contacting a substrate having palladium tin catalyst at its surface with the present accelerator solution. Any method can be used in order to bring about such contact between the substrate and the accelerator solution. For example, a method can be used wherein the substrate is immersed in the accelerator solution, or a method can be used wherein the accelerator solution is sprayed on the substrate. The bath temperature and treatment time can be set appropriately based on known conventional parameters.

[0021] The palladium tin catalyst used in such electroless copper plating method can be any palladium tin catalyst. The catalyst that is used typically has the form of a catalyst liquid in which the palladium tin catalyst is present as colloid in a medium.

[0022] Substrates that can be used in the present method can be composed of any resin, provided that the substrate has physical properties suitable to the objective for which it is used, such as strength and corrosion resistance. Substrates of any shape may be used without particular restrictions. It is preferable for the substrate to be a resin substrate, and resin substrates are not restricted to resin moldings, as they may also be composite materials formed by the interposition of a resin reinforcing material such as glass fiber reinforcing between resin layers. Alternatively, substrates can be used that are produced by the formation of a thin film of resin on a substrate composed of ceramic, glass, metal or various other members. The resin substrate can be composed of a single resin, or can be composed of multiple resins. In addition, a composite material can be formed by the application or lamination of resin on another substrate.

[0023] In the electroless copper plating method of the present invention, palladium tin catalyst is first affixed to the substrate. Any method can be used as the method for affixing catalyst, provided that the method fixes the catalyst on the substrate. For example, methods that may be cited involve the immersion of a substrate in the catalyst liquid or spraying of catalyst liquid on the substrate, but examples are not restricted to these. The substrate can be subjected, for example, to an immersion or spraying treatment in a commonly used conditioner as necessary prior to affixing the catalyst. Thus, a conditioning treatment, etching treatment or other such treatment can be carried out in order to facilitate affixing of the palladium or palladium tin catalyst on the substrate.

[0024] In the electroless copper plating method of the present invention, metallic palladium is produced on the substrate by means of the accelerator treatment, and such metallic palladium functions as active catalyst nuclei for deposition of metallic copper during electroless copper plating. During electroless copper plating, a copper thin film is directly formed on the resin substrate, thus producing a copper-resin composite material. While not intending to be bound by theory, it is thought that roughening of the deposited copper layer following the electroless copper plating treatment is prevented by the use of the present accelerator solution, because an increase in turbidity of the accelerator solution is prevented. As discussed above, this increase in turbidity of the accelerator solution is thought to be one of the causes of roughening. The aforementioned electroless copper plating method can be a copper sulfate plating method, copper cyanide plating method, copper pyrophosphate plating method or any well-known electrolytic copper plating method, but copper sulfate plating is preferred.

[0025] The present invention is described in additional detail below by the examples, but the scope of the present invention is not restricted by such examples.

Examples

Comparative Example 1

Suspension of accelerator solution with palladium tin catalyst

[0026] Methanesulfonic acid and a nonionic surfactant were dissolved in purified water at concentrations of 48 g/L and 7.35 g/L respectively, thus producing an accelerator solution. Palladium tin catalyst suspension (0.15 g/L elemental palladium, 3.9 g/L elemental tin) was added to 200 mL of the accelerator solution so that the volume ratio was 0% (not added), 0.5% (final accelerator solution palladium concentration: 0.75 mg/L, tin concentration: 19.5 mg/L), 1.0% (final accelerator solution palladium concentration: 1.5 mg/L, tin concentration: 39 mg/L), 1.5% (final accelerator solution palladium concentration: 2.25 mg/L, tin concentration: 58.5 mg mg/L) or 5.0% (final accelerator solution palladium concentration: 7.5 mg/L, tin concentration: 195 mg/L), and the solution was stirred for 1 hr. (catalyst concentration 0-1.5%) or was stirred for 1 hr. and allowed to stand for 18 hr. (catalyst concentration 5%). The turbidity of said accelerator solution was then measured. Measurement of turbidity was carried out using a turbidity meter (HACH; model 2100A), and the results were expressed in NTU units (nephelometric turbidity units; in JIS K 0101-1988 "Industrial Water Test Methods" section 9.2, transmissive turbidity is turbidity determined using a formazin standard solution, where the formazin standard solution indicated as "400-level formazin" in said literature corresponds to 400 NTU).

Example 1

Effect of suspension inhibition due to accelerator solution suspension inhibiting compound

[0027] The accelerator solution suspension inhibiting compounds shown in Table 1 were added at the concentrations indicated in Table 1 to an accelerator solution having the composition shown in Comparative Example 1, to produce the accelerator solutions of this Example. The turbidity of the accelerator solutions was measured by the same method as in Comparative Example 1.

Comparative Example 2

Compound not exhibiting suspension inhibition effect

[0028] The compounds shown in Table 1 were added in the concentrations indicated in Table 1 to the accelerator solution of Example 1, thus producing the accelerator solutions of this Example. The accelerator solutions were then subjected to turbidity measurement using the same method as in Comparative Example 1.

[0029] The results of Comparative Examples 1 and 2 and Example 1 are presented in Table 1.

Table 1

Example	Compound No.	Added Compound	Compound Concentration	Turbidity (NTU)				
				Catalyst concentration				
				0%	0.5%	1.0%	1.5%	5.0%
C.E. 1	-	None	-	-	1.23	1.3	2.57	11.8
W.E. 1	1	L-Cysteine	5g/L	0.152	0.155	0.148	0.15	0.108
	2	L-Cystine	10g/L	0.173	0.204	0.182	0.182	0.223
	3	Hydroxyethylidene diphosphonic acid	10g/L	0.097	0.17	0.214	0.224	2.76
	4	Thiomalic acid	5g/L	0.222	0.198	0.177	0.241	0.206
	5	Aminopyrazine	5g/L	0.222	0.234	0.264	0.248	16.4
	6	Ascorbic acid	5g/L	0.135	0.13	0.206	0.262	12.8
	7	Hydroquinone	5g/L	0.137	0.23	0.302	0.414	4.28
	8	3-Amino-1,2,4-triazole	5g/L	0.552	0.588	0.594	0.64	9.7
	9	DL-Methionine	10g/L	0.115	0.118	0.314	0.677	29.9
	10	Thiourea	10g/L	0.291	0.535	0.59	0.802	3.57
	11	Phosphoric acid	10g/L	0.116	0.429	1.05	1.11	14
	12	Thiodisuccinic acid	5g/L	1.3	1.27	1.23	1.16	0.842
	13	Oxalic acid	5g/L	0.17	0.874	0.815	1.21	1.18
	14	Urea	5g/L	0.157	1.51	3.3	2.04	0.902
	15	Adenine	5g/L	0.197	0.329	0.354	2.25	29
	16	Guanidine nitrate	5g/L	0.175	1.69	2.71	2.34	1.16
	17	Sodium tetraborate decahydrate	5g/L	0.105	1.65	2.45	2.42	3.4
	18	Hydroxyacetic acid	10g/L	0.15	2.72	3.89	2.46	3.81
	19	Cystamine sulfate	5g/L	0.231	1.36	2.66	2.55	-
	20	Boric acid	5g/L	0.15	1.45	2.2	2.64	3.23
	21	Sodium o-toluidine-4-sulfonate	10g/L	0.78	2.53	2.59	2.72	4.91
	22	S-2-Pyrrolidonecarboxylic acid	5g/L	0.146	2.72	2.18	2.8	3.4
	23	Glyoxylic acid monohydrate	5g/L	0.121	2.3	3.56	3.27	3.72
	24	Lactic acid	10g/L	0.125	3.04	4.57	3.29	3.58
	25	Allantoin	2.5g/L	0.253	1.89	2.94	3.47	5.74
	26	Phosphorous acid	5g/L	0.149	0.876	2.22	3.75	-
	27	Itaconic acid	5g/L	0.198	2.16	3.31	4.68	6.22
	28	2-Amino-5-methyl-1,3,4-thiadiazole	5g/L	0.262	1.72	3.94	5.67	9.14
	28	2-Amino-5-methyl-1,3,4-thiadiazole	10g/L	0.396	0.426	0.425	9.1	12.3
	29	1,3-Phenylenediamine-4-sulfonic acid	10g/L	0.997	6.3	6.3	6.63	8.53
	30	Hydroxylamine nitrate	5g/L	0.128	0.132	6.04	6.68	-
	31	Hydrazinium sulfate	5g/L	0.237	3.92	7.15	7.55	6.39
	32	Sulfosalicylic acid	10g/L	0.18	0.224	0.274	7.74	11.4
	33	Phenolsulfonic acid	10g/L	0.122	0.628	2.29	7.94	31.3
	34	1-(2,3-Dihydroxypropyl)-benzotriazole	5g/L	0.471	1.14	6.92	9.94	35.4
	35	2-Imidazolidinone	5g/L	0.174	0.149	1.29	14	-
C.E. 2	36	Amidosulfuric acid	10g/L	0.19	2.33	3.62	3.62	16.8
	37	Glycine	10g/L	0.15	2.51	5. 29	3.63	16.6
	38	p-Toluenesulfonic acid	10g/L	0.211	2.16	4.34	3.82	16.8
	39	Persulfite	10g/L	0.13	1.55	2.74	3.94	13.5
	40	Allylthiourea	5g/L	0.828	2.75	4	4.43	28.2
	41	Nicotinic acid	10g/L	0.417	1.25	5.58	6.77	-
	42	S-M-ethylisothiourea sulfate	10g/L	0.353	4.66	7.55	8.1	13.4
	43	Carboxymethylmercaptosuccinic acid	5g/L	0.347	5.9	10.7	13.8	26.2
	44	Thiodiglycol	10g/L	0.413	6.17	10.8	14.1	30.7

[0030] In Comparative Example 1, the turbidity of the accelerator solutions increased with increasing palladium tin catalyst concentration in the accelerator solution. Among the compounds of Example 1, on the other hand, compound nos. 1-4, 7, 8, 10 and 13 exhibited the effect of suppressing turbidity increase under all of the palladium tin catalyst concentrations that were investigated.

[0031] In addition, although inhibition of turbidity increase was not seen with all of the concentrations with the other compounds of Example 1, inhibition of the increase in turbidity was seen with specific palladium tin catalyst concentrations. In contrast, with the compounds of Comparative Example 2, no effect of inhibiting turbidity increase was seen at any of the palladium tin catalyst concentrations.

[0032] From these results, it is clear that the accelerator solution suspension inhibiting compounds of the present

invention inhibit turbidity increase in accelerator solutions caused by palladium tin catalyst.

Example 2

Effect of turbidity inhibition due to accelerator solution suspension inhibiting compound

[0033] The concentrations of thiomalic acid, cysteine, cystine, hydroxyethylidene diphosphonic acid and thiodisuccinic acid were varied, and inhibitory effects on turbidity increase in accelerator solutions were investigated. Testing was carried out in the same manner as in Example 1 above, with the exception that the concentrations of the respective compounds, the palladium tin catalyst concentration and the stirring time were varied. The stirring time was 1 hr. for catalyst concentrations of 0-1.5%, and the stirring time was 1 hr., followed by 18 hr. of rest, for catalyst concentrations of 5% or greater.

[0034] The results are shown in Table 2. In Table 2, Comparative Example 1 above is presented as a control.

Table 2

Example	Compound no.	Added compound	Compound concentration	Turbidity (NTU)											
				Catalyst concentration											
				0%	0.5%	1.0%	1.5%	2.0%	3.0%	4.0%	5.0%	6.0%	10%	15%	20%
C.E. 1	-	None	-	-	1.23	1.3	2.57				11.8				
W.E. 2	4	Thioglycolic acid	5g/L	0.226	0.196	0.182	-	0.172	0.165	0.185	0.195	0.172	0.141	0.143	0.145
	4	Thioglycolic acid	1g/L	0.134	0.171	0.162	-	0.193	0.208	0.19	0.185	0.201	0.163	0.186	0.212
	4	Thioglycolic acid	0.5g/L	0.162	0.126	0.142	-	0.192	0.201	0.168	0.186	0.177	0.2	0.171	0.282
	4	Thioglycolic acid	0.25g/L	0.135	-	0.119	-	0.148	0.136	0.156	0.158	0.284	0.191	0.182	0.163
	4	Thioglycolic acid	0.1g/L	0.153	-	0.127	-	0.153	0.115	0.146	0.143	0.154	0.198	0.103	0.123
	4	Thioglycolic acid	0.05g/L	0.144	-	0.123	-	0.142	0.124	0.101	0.121	0.106	0.104	0.111	0.816
	4	Thioglycolic acid	0.01g/L	0.163	-	0.136	-	0.171	0.161	0.154	0.207	0.223	2.03	7.44	-
	4	Thioglycolic acid	0.005g/L	0.155	-	0.152	-	0.178	0.225	0.206	0.273	0.421	11.8	-	-
	4	Thioglycolic acid	0.001g/L	0.171	-	0.221	-	1.49	4.55	5.54	5.18	5.03	-	-	-
	1	L-cysteine	5g/L	0.167	0.168	0.186	-	0.186	0.143	0.13	0.167	0.153	0.152	0.143	0.142
	1	L-cysteine	1g/L	0.104	0.142	0.115	-	0.183	0.218	0.192	0.278	0.243	0.342	0.273	0.222
	1	L-cysteine	0.5g/L	0.145	0.13	0.1	-	0.087	0.137	0.125	0.142	0.127	0.194	0.37	0.222
	1	L-cysteine	0.25g/L	0.153	-	0.111	-	0.246	0.26	0.222	0.257	0.301	0.31	0.251	0.313
	1	L-cysteine	0.1g/L	0.12	-	0.165	-	0.167	0.159	0.171	0.181	0.184	0.169	0.28	0.208
	1	L-cysteine	0.05g/L	0.146	-	0.208	-	0.252	0.329	0.353	0.351	0.34	0.423	0.304	0.537
	2	L-cysteine	5g/L	0.16	-	0.125	-	0.157	0.2	0.431	2.42	0.219	1.03	-	-
	2	L-cysteine	1g/L	0.12	-	0.164	-	0.374	3.98	10.9	16.5	-	-	-	-
	2	L-cysteine	0.5g/L	0.11	-	0.134	-	0.257	4.43	11.7	16.7	-	-	-	-
	3	Hydroxyethylidene diphosphonic acid	5g/L	0.115	-	0.114	-	0.346	0.411	0.805	0.979	6.8	-	-	-
	3	Hydroxyethylidene diphosphonic acid	1g/L	0.155	-	0.139	-	0.152	0.182	0.152	0.214	5.82	-	-	-
	3	Hydroxyethylidene diphosphonic acid	0.5g/L	0.143	-	0.151	-	0 169	0.559	0.67	0.685	2.48	-	-	-
	12	Thiodisuccinic acid	1g/L	0.488	-	0.592	-	0 462	0.397	0.429	0.442	0.531	0.437	2.13	-
	12	Thiodisuccinic acid	0.5g/L	0.291	-	0.553	-	0.342	0.35	0.326	0.358	0.403	0.542	1.21	-
	12	Thiodisuccinic acid	0.1g/L	0.174	-	0.663	-	0.443	0.434	0.521	0.615	0.638	5.78	10.6	-

[0035] An increase in turbidity inhibition effect was seen along with increase in compound concentration for all of the compounds evaluated in Example 2. In addition, a trend towards increasing accelerator solution turbidity was found along with increasing palladium tin catalyst concentration.

Comparative Example 3

Adsorption of palladium tin catalyst on substrate

[0036] The copper foil of a copper-clad laminate board was etched away to produce a substrate (epoxy resin substrate FR-4; manufactured by Hitachi Kasei Kogyo; MCL-E-67), which was then cut to a square of 5 cm. After drying, the size of the substrate was measured. After size measurement, the substrate was treated for 5 min in a cleaner/conditioner, and was then warmed for 1 min, followed by rinsing with water for 1 min. The material was then treated for 1 min with 10% sulfuric acid, and was rinsed with water for 2 min. the substrate was then treated for 1.5 min with pre-dip liquid, and was then immersed for 5.5 min in a palladium tin catalyst solution containing 0.15 g/L of palladium and 3.9 g/L of tin. After the catalyst affixing treatment, the substrate was rinsed with water for 2 min, and the substrate was then immersed in a 30°C accelerator solution. The substrate was removed after 5.5 or 8 min, and the amount of elemental palladium and tin present on said substrate was measured with a high-frequency induction-coupled plasma analyzer. The accelerator solution was produced by dissolving methanesulfonic acid at a concentration of 48 g/L, and nonionic surfactant at a concentration of 7.35 g/L, in purified water.

[0037] The method for measuring the amount of palladium or tin adsorbed on the substrate was carried out as described below. About 8 mL of aqua regia was added to substrate that had been treated as described above, and the solution was heated. After boiling, the resulting substrate solution was transferred into a graduated flask, and was adjusted to 100 mL using purified water. The substrate solution was then analyzed with a high-frequency induction-coupled plasma analyzer, and the palladium and tin amounts were quantified. The amount of tin or palladium adsorbed on the substrate was expressed as the amount of palladium or tin per unit surface area of substrate ($\mu g/cm^2$).

Example 3

Effect of accelerator solution suspension inhibiting compound of the present invention on adsorption of palladium tin catalyst on substrate

[0038] Accelerator solutions and substrate having adsorbed palladium tin catalyst were prepared using the same method as in Comparative Example 3, with the exception that thiomalic acid, cysteine, phosphoric acid, hydroxyacetic acid, hydroquinone, ascorbic acid or aminopyrazine at the concentration indicated in Table 3 was added to the accelerator solution of Comparative Example 3. The amount of palladium or tin present on the substrate after the accelerator treatment was measured using the same method.

[0039] The results of Comparative Example 3 and Example 3 are shown in Table 3. In the table, the residual ratio is a value that expresses the percentage of the amount of palladium or tin after treatment, taking the amount of palladium or tin prior to the accelerator treatment as 100%. The reason that the amounts of palladium and tin are different before treatment is that the amounts were evaluated using separate experiments.

Table 3

Example	Added amount (amount)	Pd adsorption 0 min Pd adsorption $\mu g/cm^2$	Residual ratio (%)	5.5 min Pd adsorption $\mu g/cm^2$	Residual ratio (%)	8 min Pd adsorption $\mu g/cm^2$	Residual ratio (%)	Sn adsorption 0 min Sn adsorption $\mu g/cm^2$	Residual ratio (%)	5.5 min Sn adsorption $\mu g/cm^2$	Residual ratio (%)	8 min Sn adsorption $\mu g/cm^2$	Residual ratio (%)
C.E. 3		1.37	100	0.77	56	0.7	51	3.06	100	1.01	33	0.93	30
3	Thiomalic acid 5 g/L	1.37	100	1.06	77	1.09	80	3.06	100	1.63	53	1.43	47
	Thiomalic acid 0.05 g/L	1.37	100	1.35	99	1.54	112	3.06	100	2.15	70	2.06	67
	L-Cysteine 5 g/L	1.37	100	1.09	80	0.88	64	3.06	100	1.76	58	1.29	42
	L-Cysteine 0.1 g/L	1.37	100	1.30	95	1.03	75	3.06	100	2.18	71	1.55	51
	Phosphoric acid 8.5 g/L	1.13	100	1.05	93	-	-	2.85	100	2.79	98	-	-
	Hydroxyacetic acid 10 g/L	1.13	100	0.53	47	-	-	2.85	100	0.15	5	-	-
	Hydroquinone 5 g/L	1.13	100	1.06	94	-	-	2.85	100	1.13	40	-	-
	Ascorbic acid 5 g/L	1.13	100	1.25	111	-	-	2.85	100	1.51	53	-	-
	Aminopyrazine 5 g/L	1.13	100	0.63	56	-	-	2.85	100	0.84	29	-	-

[0040] As is clear from the results of Comparative Example 3, the amount of tin present on the substrate deceased due to the acceleration treatment, and the amount of palladium decreased slightly, although a certain quantity remained. This result suggests that the tin is released from the substrate due to an oxidation reduction reaction between palladium and tin during the accelerator treatment. As a result, the palladium remaining on the substrate is present in the form of metallic palladium that can function as active catalyst nuclei in the electroless copper plating treatment.

[0041] In addition, when thiomalic acid, L-cysteine, ascorbic acid or hydroquinone was added, the amount of elemental tin remaining on the substrate decreased, which suggests that the oxidation reduction reaction is occurring between the palladium and tin. In conjunction therewith, the decrease in amount of palladium remaining on the substrate was controlled relative to Comparative Example 3. Based on these results, it is thought that these compounds control release of palladium into the accelerator solution, and that these compounds thus have superior suspension inhibition effects and superior effects in terms of the effective formation of palladium catalyst nuclei.

[0042] Moreover, for hydroxyacetic acid and aminopyrazine, a decrease in tin and palladium was seen that was at the same level as in Comparative Example 3. This result suggests that an oxidation reduction reaction between palladium and tin occurs in the accelerator treatment, and the palladium element remaining on the substrate is present in the form of metallic palladium that can function as active catalyst nuclei in the electroless copper plating treatment.

[0043] On the other hand, almost no decrease in tin was found with phosphoric acid, which suggests that the capacity for the accelerator solution to function as an accelerator is weak when the solution contains phosphoric acid.

Example 4

Effect of thiomalic acid on the adsorption of palladium tin catalyst on substrate

[0044] The adsorption amount of palladium and tin on substrate after accelerator treatment was measured using the same method as in Example 3, with the exception that thiomalic acid was used as accelerator solution suspension inhibiting compound, and the concentration was varied.

Comparative Example 4

[0045] The adsorption amount of palladium and tin on substrate after accelerator treatment was measured using the same method as in Example 4, with the exception that accelerator solution suspension inhibiting compound was not contained in the accelerator solution.

Comparative Example 5

[0046] The adsorption amount of palladium and tin on substrate after accelerator treatment was measured using the same method as in Example 4, with the exception that an accelerator solution was used that contained sulfuric acid at a concentration of 0.25 mol/L, which is a solution that is known to accelerate palladium tin catalyst.

[0047] The results of Example 4 and Comparative Examples 4 and 5 are shown in Table 4.

Table 4

Example	Added amount (amount)	Pd adsorption 0 min Pd adsorption $\mu g/cm^2$	Residual ratio (%)	5.5 min Pd adsorption $\mu g/cm^2$	Residual ratio (%)	8 min Pd adsorption $\mu g/cm^2$	Residual ratio (%)	Sn adsorption 0 min Sn adsorption $\mu g/cm^2$	Residual ratio (%)	5.5 min Sn adsorption $\mu g/cm^2$	Residual ratio (%)	8 min Sn adsorption $\mu g/cm^2$	Residual ratio (%)
C.E. 4		1.22	100	0.88	72	0.64	52	2.92	100	1.17	40	0.96	33
4	Thiomalic acid	1.22	100	1.28	105	1.01	83	2.92	100	1.69	58	1.28	44
	Thiomalic acid	1.22	100	1.05	86	1.15	94	2.92	100	1.7	58	1.68	58
	Thiomalic acid	1.22	100	1.13	93	1.23	101	2.92	100	1.85	63	2.09	72
	Thiomalic acid	1.22	100	1.11	91	1.19	98	2.92	100	1.79	61	2.01	69
C.E. 5	H_2SO_4 0.25 mol/L	1.22	100	0.60	49	0.47	39	2.92	100	0.96	33	0.58	20

[0048] As is clear from Example 4, a retaining effect with respect to residual palladium and a reduction effect with respect to residual elemental tin amount were manifested starting at a thiomalic acid concentration of 0.002 g/L.

[0049] When sulfuric acid was used, a decrease in palladium amount was found along with a decrease in residual elemental tin.

Example 5

Effect of thiomalic acid on adsorption of palladium tin catalyst on substrate

[0050] The adsorption amount of palladium and tin on a substrate after accelerator treatment was measured using the same method as in Example 4, with the exception that the accelerator solution treatment time and the thiomalic acid concentration were varied, and the temperature of the accelerator solution was set at 40°C or 30°C.

Comparative Example 6

[0051] The adsorption amount of palladium and tin on substrate after accelerator treatment was measured using the same method as in Example 5, with the exception that accelerator solution suspension inhibiting compound was not contained.

[0052] The results for Example 5 and Comparative Example 6 are presented in Table 5.

Table 5

Example	Bath temperature °C	Added amount of thiomalic acid	Pd adsorption 0 min		3 min		5.5 min		8 min	
			Pd adsorption $\mu g/cm^2$	Residual ratio (%)	Pd adsorption $\mu g/cm^2$	Residual ratio (%)	Pd adsorption $\mu g/cm^2$	Residual ratio (%)	Pd adsorption $\mu g/cm^2$	Residual ratio (%)
C.E. 6	30	-	1.45	100	1.19	82	0.66	46	0.58	40
5	30	0.01g/L	1.45	100	1.44	99	1.37	94	1.26	87
	30	0.05g/L	1.45	100	1.40	97	1.39	96	1.2	83
	30	0.1g/L	1.45	100	1.31	90	1.44	99	1.24	86
C.E. 6	40	-	1.45	100	0.74	51	0.44	30	0.42	29
5	40	0.01g/L	1.45	100	1.26	87	1.16	80	1.24	86
	40	0.05g/L	1.45	100	1.38	95	1.25	86	1.23	85
	40	0.1g/L	1.45	100	1.32	91	1.22	84	1.17	81
	Bath temperature °C	Added amount of thiomalic acid	Sn adsorption 0 min		3 min		5.5 min		8 min	
			Sn adsorption $\mu g/cm^2$	Residual ratio (%)	Sn adsorption $\mu g/cm^2$	Residual ratio (%)	Sn adsorption $\mu g/cm^2$	Residual ratio (%)	Sn adsorption $\mu g/cm^2$	Residual ratio (%)
C.E. 6	30	0.01g/L	3.46	100	2.31	67	1.96	57	1.68	49
5	30	0.05g/L	3.46	100	2.11	61	1.93	56	1.62	47
	30	0.1g/L	3.46	100	1.99	58	2.07	60	1.67	48
	40	-	3.46	100	1.05	30	0.41	12	0.35	10
C.E. 6	40	0.01g/L	3.46	100	1.93	56	1.59	46	1.64	47
5	40	0.05g/L	3.46	100	1.94	56	1.73	50	1.58	46
	40	0.1g/L	3.46	100	1.77	51	1.41	41	1.23	36

[0053] As is clear from Comparative Example 6, regardless of whether the bath temperature was 30°C or 40°C, a decrease in residual tin amount and a decrease in residual palladium amount were observed starting at an accelerator solution treatment time of 3 min.

[0054] As is clear from Example 5, a decrease in residual tin amount was seen at a treatment time of 3 min, regardless of whether the bath temperature was 30°C or 40°C, and in addition, the palladium retaining effect was improved relative to Comparative Example 6.

Example 6

Investigation of adsorption effects in accelerator solutions containing tin element

[0055] A solution was prepared by using 0.05 g/L of thiomalic acid as the accelerator solution suspension inhibiting compound, and adding palladium tin catalyst solution to the accelerator solution. The added palladium tin catalyst solution was a solution containing palladium and tin at a weight ratio of 7:10,000, and the added amount was 0-10 mg/L in terms of tin concentration in the solution. The bath temperature was 30°C and the treatment time was 5.5 min. With these exceptions, the adsorption amount of palladium and tin on a substrate after accelerator treatment was measured using the same method as in Example 5.

Comparative Example 7

[0056] The adsorption amount of palladium and tin on a substrate after accelerator treatment was measured using the same method as in Example 6, with the exception that thiomalic acid was not contained.

[0057] The results for Example 6 and Comparative Example 7 are shown in Table 6.

Table 6

Example	Amount of thiomalic acid added	Pd adsorption amount after catalyst affixing treatment	Amount of adsorbed Pd after accelerator treatment									
			Sn 0 μg/L Pd adsorption $\mu g/cm^2$	Residual ratio (%)	Sn 5 μg/L Pd adsorption $\mu g/cm^2$	Residual ratio (%)	Sn 10 μg/L Pd adsorption $\mu g/cm^2$	Residual ratio (%)	Sn 20 μg/L Pd adsorption $\mu g/cm^2$	Residual ratio (%)	Sn 30 μg/L Pd adsorption $\mu g/cm^2$	Residual ratio (%)
C.E. 7	-	1.35	0.80	59	1.25	93	1.33	99	1.35	100	1.30	96
6	0.05g/L	1.35	1.28	95	1.21	90	1.30	96	1.31	97	1.33	99
	Amount of thiomalic acid added	Sn adsorption amount after catalyst affixing treatment	Sn 0 μg/L Sn adsorption $\mu g/cm^2$	Residual ratio (%)	Sn 5 μg/L Sn adsorption $\mu g/cm^2$	Residual ratio (%)	Sn 10 μg/L Sn adsorption $\mu g/cm^2$	Residual ratio (%)	Sn 20 μg/L Sn adsorption $\mu g/cm^2$	Residual ratio (%)	Sn 30 μg/L Sn adsorption $\mu g/cm^2$	Residual ratio (%)
C.E. 7	-	3.25	1.02	31	1.94	60	2.28	70	2.34	72	2.62	81
6	0.05g/L	3.25	1.96	60	1.95	60	2.07	64	2.07	64	2.37	73

[0058] In Example 6 and Comparative Example 7, tin and palladium were added to the accelerator solution. Actually, because the amount of tin and palladium in the bath increases when the use of accelerator solution was stopped, this test system is used as a model for accelerator solutions that are used for a determinate time period.

[0059] The added amount of catalyst was changed in Comparative Example 7, and the amount of residual palladium present after treatment varied. On the other hand, even when the added amount of catalyst was changed in Example 6, there was almost no observed change in the residual amount of palladium. Ordinarily, when an accelerator bath is used in an industrial setting, the solution is exchanged when the tin concentration in the solution reaches about 30 mg/L, although this will differ depending on parameters of use and other considerations. For this reason, it is desirable for the amount of adsorbed palladium not to vary when the tin concentration is in the range of 0-30 mg/L. The accelerator solution of the present invention has a constant adsorbed palladium amount over this range, and it is clear that changes in the palladium amount adhered to the substrate will be controlled, even when the tin content and palladium content vary during use in an industrial setting.

[0060] As described above, the accelerator bath of the present invention contains accelerator solution suspension inhibiting compound, and as a result, it has the effect of inhibiting or reducing an increase in accelerator solution turbidity when use is interrupted, which has been a problem with conventional accelerator solutions. In addition, by controlling the increase in turbidity in this manner, an effect is produced whereby it is possible to prevent roughening of deposited copper layers in copper-resin composite materials obtained by electrolytic copper plating treatments carried out after electroless copper plating. This is particularly true for electrolytic copper plating treatments that have low leveling capacity.

[0061] In addition, the accelerator solution of the present invention has the effect of preventing a decrease in the adsorbed amount of palladium catalyst.

Claims

1. An additive for accelerator solutions comprising accelerator solution suspension-inhibiting compounds selected from the group consisting of one or more cysteine, cystine, thiomalic acid, methionine, thiodisuccinic acid, oxalic acid, hydroxyacetic acid, glyoxylic acid, lactic acid, itaconic acid, 2-pyrrolidone-5-carboxylic acid, ascorbic acid, hydroquinone, aminopyrazine, 3-amino-1H-1,2,4-triazole, thiourea, urea, adenine, guanidine, allantoin, 2-amino-5-methyl-1,3,4-thiadiazole, hydroxylamine, cystamine, hydrazine, 1-(2,3-dihydroxypropyl)benzotriazole, 2-imidazolidinone, o-toluidine-4-sulfonic acid, 1,3-phenylenediamine-4-sulfonic acid, sulfosalicylic acid, phenolsulfonic acid, phosphoric acid, phosphonic acid, hydroxyethylidene diphosphonic acid, boric acid, tetraboric acid and salts of these compounds.

2. The additive for accelerator solutions, of claim 1 further comprising one or more acids other than the accelerator solution suspension-inhibiting compounds and optionally one or more nonionic surfactants.

3. An accelerator solution comprising one or more accelerator solution suspension-inhibiting compounds selected from the group consisting of cysteine, cystine, thiomalic acid, methionine, thiodisuccinic acid, oxalic acid, hydroxyacetic acid, glyoxylic acid, lactic acid, itaconic acid, 2-pyrrolidone-5-carboxylic acid, ascorbic acid, hydroquinone, aminopyrazine, 3-amino-1H-1,2,4-triazole, thiourea, urea, adenine, guanidine, allantoin, 2-amino-5-methyl-1,3,4-thiadiazole, hydroxylamine, cystamine, hydrazine, 1-(2,3-dihydroxypropyl)benzotriazole, 2-imidazolidinone, o-toluidine-4-sulfonic acid, 1,3-phenylenediamine-4-sulfonic acid, sulfosalicylic acid, phenolsulfonic acid, phosphoric acid, phosphonic acid, hydroxyethylidene diphosphonic acid, boric acid, tetraboric acid and salts of these compounds, and one or more acids other than the aforementioned accelerator solution suspension-inhibiting compounds.

4. The accelerator solution of claim 3 wherein the acid other than the accelerator solution suspension-inhibiting compounds is an alkylsulfonic acid.

5. The accelerator solution of claim 3 further comprising one or more nonionic surfactants.

6. The accelerator solution of claim 3 wherein the accelerator solution suspension-inhibiting compound is present at a concentration of 1 mg/L to 50 g/L.

7. A method for electroless copper plating comprising the steps of: affixing a palladium tin catalyst on a substrate, contacting the substrate with the accelerator solution of claim 3, and then contacting the substrate with an electroless copper plating bath.

8. The method of claim 7 wherein the accelerator solution further comprises one or more nonionic surfactants.

9. The method of claim 7 wherein the accelerator solution further comprises one or more acids other than the accelerator solution suspension-inhibiting compounds.