

Acidic Bath for Electrolytically Depositing a Copper Deposit Containing Halogenated or pseudohalogenated monomeric phenazinium compounds

Specification:

5

The invention relates to halogenated or pseudohalogenated monomeric phenazinium compounds, to a method of preparing same, to an acidic bath containing said compounds for electrolytically depositing a copper deposit as well as to a method of electrolytically depositing a copper deposit using said acidic bath. The halogenated or pseudohalogenated monomeric phenazinium compounds may be used as additives in copper plating baths to more specifically form mirror bright level deposits of copper in order to produce decorative surfaces. The compounds may moreover be used as additives in copper plating baths to selectively and completely fill with copper blind microvias in printed circuit boards and trenches and vias on semiconductor wafers. The compounds may also be utilized as additives in copper plating baths for depositing copper onto semiconductor substrate surfaces provided with recesses during the manufacturing process of integrated circuits, with the entire semiconductor substrate surface being uniformly coated with copper.

10

15

20

25

For depositing bright copper surfaces, organic additives are usually added in small quantities to most of the acidic copper electrolytes in order to obtain bright copper layers instead of a crystalline matte deposit. In this approach, an additive compound or a combination of several additive compounds such as polyethylene glycols, thioureas and the derivatives thereof, thio hydantoin, thio carbamic acid esters as well as thio phosphoric acid esters is often added. Nowadays however, the additives mentioned are no longer significant, due to the fact that the quality of the thus obtained copper layers meets by no means today's requirements. The thus obtained coatings are either too brittle or exhibit poor brightness and insufficient leveling.

30

The utilization of certain phenazinium compounds such as phenazine dyestuffs *e.g.*, safranines and of the derivatives thereof, that are also used as paper and leather dyes and as dyes for keratin-containing fibers, has long been known for producing bright copper layers. In accordance with DE-PS 947 656, these dyes, *e.g.*, dimethyl safranine azo dimethyl aniline, diethyl safranine azo dimethyl aniline, Janus grey and

safranine azo naphthol are being used as the only additives. It is moreover known to use said compounds in combination with other additives as well.

Further, DE-AS 1 521 062 suggests bath compositions containing an organic sulfide
5 that contains at least one sulfonic acid group as well as, mixed thereto or chemically bonded, a polyether that contains at least three, preferably six, oxygen atoms and is free of aliphatic hydrocarbon chains having more than six C-atoms. These baths permit deposition of smooth, bright and ductile copper layers. Preferred polyethers mentioned are 1,3-dioxolane polymerisates having a molecular weight of at least
10 296, preferably of about 5000. Phenazine dyestuffs may also be utilized in combination with the bath additives mentioned, for example diethyl phenosafranine azo dimethyl aniline, dimethyl phenosafranine azo dimethyl aniline, diethyl phenosafranine azo phenol and dimethyl azo-(2-hydroxy-4-ethylamino-5-methyl)-benzene. The phenazine dyestuffs permit high leveling and a wide range of bright
15 deposits.

With the copper electrolytes described in DE-AS 1 521 062 however it is not possible to utilize a higher cathodic current density. Moreover, the deposited copper surfaces can only be nickel-plated after having been subjected to a preliminary intermediate
20 treatment.

It is further known to use hydroxylated and halogenated phenazine dyestuffs of the safranine type as levelers and brighteners, such as DE-OS 2 028 803. This document relates to polymeric phenazinium compounds, the phenazinium skeletale
25 structure being substituted with hydrogen, lower alkyl or substituted or unsubstituted aryl.

1973:43420 CAPLUS relating to A.Ya. Il'chenko and V.N. Rudenko in: Khimiya Geterotsiklicheskikh Soedinenii (1972), (10), 1425-1429 schematically discloses the
30 synthesis of 3-chloro-5-methyl-7-(phenylamino)-phenazinium perchlorate.

The use and production of monomeric halogenated phenazine dyestuffs for acidic copper baths is *i.a.* described In the Patent Abstracts of Japan corresponding to JP 60-056086 A. The dyestuffs are prepared in a two-stage synthesis consisting of a

diazotization reaction and of a halogenation reaction. For diazotization, the corresponding safranine dyestuff is first dissolved in the heat and filtered. At a temperature of 0 to 5°C, it is then diazotized with sodium nitrite and later hydrochloric acid being added before it is finally heated. Once it has cooled down, the reaction solution is reacted at room temperature over a period of 10 hours in the presence of copper(II) chloride solution, copper powder and hydrochloric acid to form the chlorinated phenazine dyestuff. It describes, by way of example, the preparation of 7-diethylamino-3-hydroxy-5-phenyl-phenazinium sulfate, of a mixture of 3-chloro-7-diethylamino-5-phenyl-phenazinium chloride and 7-diethylamino-3-hydroxy-5-phenyl-phenazinium chloride and of 3,7-dichloro-2,8-dimethyl-5-phenyl-phenazinium chloride.

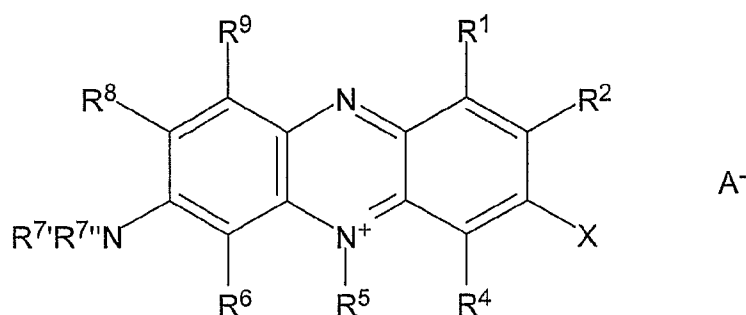
The disadvantage of the method described is that for each synthesis step, inclusive of the dissolution of the dyestuff, a separate reaction vessel is needed. As a result of the long reaction times and of the moderate stability of the diazonium compounds, which easily decompose in an acidic medium, uncontrolled reactions may take place, resulting in variable quality of the products desired. Moreover, such type of time-consuming reactions is very expensive from an economical point of view.

In order to avoid the above disadvantages of known copper baths, the object of the present invention is to more specifically provide additives by means of which particularly uniform and brilliant, meaning mirror bright, as well as leveled and ductile copper coatings may be reproducibly prepared. The additives are hereby intended to be readily synthesizable at a low cost while remaining unchanged in quality and exhibiting high purity. It further intends to enable production of mirror bright, leveled and ductile copper layers using a relatively high current density. The composition of such a copper plating bath is intended to constantly permit, during bath operation over a long period of time, to obtain copper layers having the required quality.

The present invention comprises providing halogenated or pseudohalogenated monomeric phenazinium compounds in accordance with claim 1, the method of preparing said compounds in accordance with claim 11, the acidic bath containing said compounds for electrolytically depositing a copper deposit in accordance with claim 23, the uses of the bath in accordance with the claims 27, 28 and 29 as well as

the method of electrolytically depositing a copper deposit using the acidic bath containing said compounds in accordance with claim 30. Preferred embodiments of the invention are recited in the subordinate claims.

- 5 The halogenated or pseudohalogenated monomeric phenazinium compounds of the invention can advantageously be used in a bath for electrolytically producing a mirror bright, leveled copper deposit for the purpose of forming decorative surfaces. The bath may for example be utilized for the decorative copper plating of plastic parts in the sanitary and automotive industry. Further, the compounds may also be
- 10 advantageously used in a copper plating bath for electrolytically depositing a copper deposit onto printed circuit boards with said copper deposit selectively and completely filling blind microvias in the printed circuit boards. Moreover, the compounds may also be advantageously utilized in a copper plating bath for electrolytically depositing a copper deposit onto semiconductor substrate (wafer)
- 15 surfaces provided with recesses during the manufacturing process of integrated circuits, more specifically onto surfaces having high aspect ratio recesses. The copper deposit is thereby uniformly produced on the entire semiconductor substrate surface.
- 20 The compounds of the invention are meant to be halogenated or pseudohalogenated monomeric phenazinium compounds of a purity of at least 85 mole-%, preferably of at least 90 mole-%, with a purity of at least 95 mole-% being particularly preferred and a purity of at least 98 mole-% being most preferred, having the following general chemical formula:



25

I

wherein

R^1 , R^2 , R^4 , R^6 , $R^{7'}$, $R^{7''}$, R^8 and R^9 are selected independently of each other from a group comprising hydrogen, halogen, amino, aminoalkyl, hydroxy, cyano, thiocyanate, isothiocyanate, cyanate, isocyanate, mercapto, carboxy (COO^-), the salt thereof, carbonic acid ester (COOR), sulfo (SO_3^-), the salt thereof, sulfoester (SO_3R), lower alkyl, unsubstituted aryl, substituted aryl, heteroaryl and alicyclic heteroradicals,

R^5 is selected from a group comprising lower alkyl, unsubstituted aryl, substituted aryl and heteroaryl,

X is a halogen or a pseudohalogen and

A^- is an acid anion.

The phenazinium compounds of a purity of x mole-% as mentioned herein above, herein after and in the claims refer to a mixture of the phenazinium compounds and impurities, with the phenazinium compounds being contained in the mixture at a concentration of x mole-% and the impurities at a concentration of 100 – x mole-%.

The term lower alkyl as mentioned herein above and herein after and in the claims preferably refers to C_1 - to C_4 -alkyl, meaning to methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl and *tert*-butyl. By substituted alkyl as mentioned herein above, herein after and in the claims, sulfo- or carbonic acid-substituted alkyl is preferably meant.

Aryl as mentioned herein above or herein after and in the claims preferably refers to phenyl or polycyclic aromates such as naphthyl-1 and naphthyl-2, wherein these residues may be unsubstituted or substituted respectively. If these residues are substituted, they are more specifically substituted by alkyl, preferably by lower alkyl, halogen, hydroxy, amino, wherein amino is NH_2 , NHR or $\text{NR}'\text{R}''$, wherein R, R' and R'' in turn can be lower alkyl, cyano, thiocyanate and mercapto. Phenyl may more specifically be substituted at a 2-, 4- and 6-position.

Heteroaryl as mentioned herein above or herein after and in the claims preferably refers to pyridinyl, quinolinyl and isoquinolinyl.

Alicyclic heteroradicals as mentioned herein above or herein after and in the claims
5 more specifically refer to piperidyl, piperazinyl and morpholinyl.

Carbonic acid esters (COO esters) and sulfoester (SO₃ esters) as mentioned herein above or herein after and in the claims preferably refer to carbonic acid esters of the lower alcohols such as –COOCH₃, –COOC₂H₅ and so on or to sulfonic acid esters of
10 the lower alcohols such as –SO₃CH₃, –SO₃C₂H₅ and so on, respectively. By lower alcohols C₁- to C₄- alcohols *i.e.*, methanol, ethanol, *n*-propanol, *iso*-propanol, *n*-butanol, *iso*-butanol and *tert*-butanol are meant. –COO salts and –SO₃ salts as mentioned herein after refer to carbonic acid salts and sulfonic acid salts respectively, meaning more specifically the alkali salts, earth alkali salts, aluminium
15 salts and copper salts such as –COO[–]Na⁺ or (–SO₃)₂[–] Cu²⁺.

Halogen as mentioned herein above or herein after and in the claims, more specifically in combination with the terms “hydrogen halide”, “metal halide” and “halide”, refers to fluorine, chlorine, bromine and iodine, preferably to chlorine and
20 bromine.

Pseudohalogen and pseudohalide respectively as mentioned herein above or herein after and in the claims, refer to cyanate (–OCN), thiocyanate (–SCN), isocyanate (–NCO) and isothiocyanate (–NCS).
25

Alkali metal or earth alkali metal as mentioned herein above or herein after and in the claims, for example in “salt of earth alkali metal”, preferably refers to sodium, potassium, magnesium and calcium.

30 In the phenazinium compounds of the invention, R¹, R², R⁴, R⁶, R⁷, R^{7a}, R⁸ and R⁹ are selected independently of each other from a group comprising hydrogen and lower alkyl. Alkyl may more specifically be methyl or ethyl.

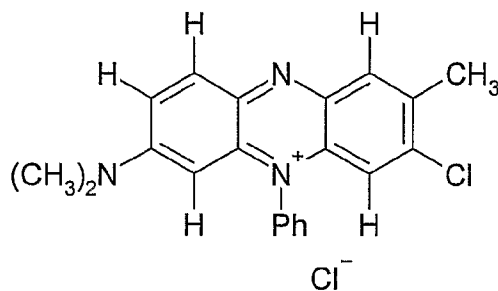
Further in the phenazinium compounds of the invention, R⁵ may preferably be aryl, more specifically phenyl.

In the compounds of the invention, X preferably is chlorine, bromine or thiocyanate.

5

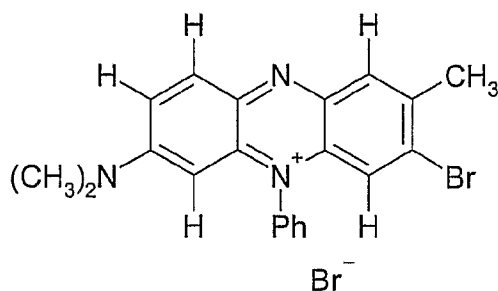
Particularly suited phenazinium compounds are selected from a group comprising halogenated phenazinium compounds, the compounds herein below being the most preferred halogenated phenazinium compounds:

- 10 i) 3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt, more specifically the chloride:

**II**

15

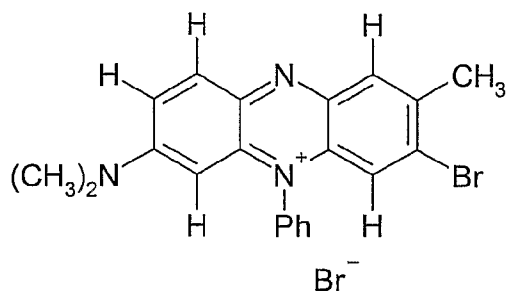
- ii) 3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt, more specifically the bromide:

**III**

20

and

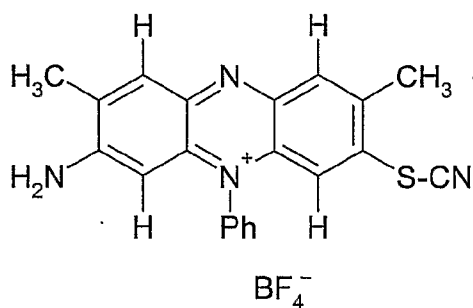
- iii) 3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium salt, more specifically the bromide:



5

as well as pseudohalogenated phenazinium compounds, the compound herein below being the most preferred pseudohalogenated phenazinium compound:

- iv) 7-amino-2,8-dimethyl-3-thiocyanato-5-phenyl-phenazinium salt, more specifically the tetrafluoroborate:



15

The compounds herein above are advantageously utilizable in an acidic copper-plating electrolyte. It has been found that the halogenated or pseudohalogenated monomeric phenazinium compounds are particularly advantageous in copper-plating baths, where they are characterized by a high plating activity.

20

Using the halogenated and pseudohalogenated monomeric phenazinium compounds of the invention in an acidic electrolytic copper-plating bath, it is possible to operate the latter at a high current density. In combination with well known other additives, it is moreover possible to achieve particularly even, brilliant copper deposits. Further,

the efficiency of the halogenated and pseudohalogenated monomeric phenazinium dyestuffs is increased by the way they are synthesized in accordance with the invention as a result of the higher purity thereof. This purity amounts to at least 85 mole-%. This means that the substances of the invention contain a maximum of 15 mole-% of impurities. These impurities may more specifically be oligomers of the phenazinium compounds, for example the dimers and trimers thereof. In adding the compounds of the invention to a copper electrolyte, one accordingly achieves perfect brilliance although the concentration of additives used is clearly lower than when using comparable known phenazinium compounds of much lower purity. Efficiency and, as a result thereof, profitability are thus considerably increased.

In contrast to the phenazinium compounds of very high purity of the invention, the compounds described in Patent Abstracts corresponding to JP 60-056086 A are of much lower purity. These substances contain a considerable fraction of oligomers of phenazinium compounds, more specifically of dimers and trimers, as can be easily experimentally proven. This fraction of impurities typically lies within the range of 40 to 50 mole-%. Accordingly, the compounds disclosed in this document are much less suited for use as additives in an electrolytic copper-plating bath than the compounds of the invention.

The halogenated monomeric phenazinium compounds set forth below:

- i) 3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt,
- ii) 3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt,
- iii) 3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium salt, and

the pseudohalogenated monomeric phenazinium compounds, preferably:

- iv) 7-amino-2,8-dimethyl-3-thiocyanato-5-phenyl-phenazinium salt,

have proved to be particularly efficient both separately and as a mixture, since they exhibit perfect brilliance both at a high and at a low current density with a much lower operative concentration being utilized in the copper electrolyte. These properties are

already achieved using all of the phenazinium compounds of the invention, although to a different extent.

The reason for the higher purity of the compounds of the invention over the phenazinium compounds disclosed in the document mentioned herein above is due to the differing methods of preparation:

Due to the two-step preparation method in several synthesis vessels (diazotization and subsequent halogenation), the preparation of halogenated monomeric compounds in accordance with JP 60-056086 A is very complicated and time-consuming, with the quality and proportion of the desired products moreover varying as a result of the low stability of the diazonium compounds with respect to the long reaction time and this in turn may result in varying efficacy of said products or product mixtures in the electrolyte.

JP 60-056086 A neither describes nor mentions the preparation of pseudo-halogenated monomeric phenazinium compounds.

Starting from monomeric phenazinium compounds of the general chemical formula **VI** given herein below, halogenated or pseudohalogenated monomeric phenazinium compounds, such as for acidic copper-plating baths, may now be selectively provided, with compounds of high purity being achievable in good yield:

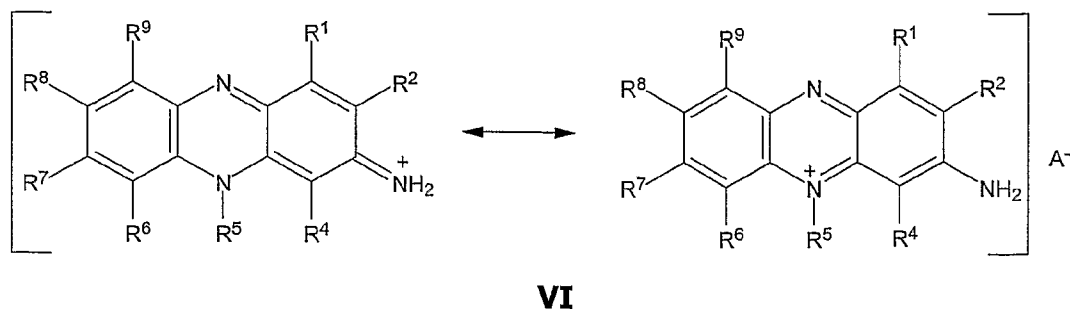
The halogenated or pseudohalogenated monomeric phenazinium compounds are synthesized using a novel preparation method. In contrast to a conventional method in which, in a first synthesis step, a diazonium compound is formed from a monomeric phenazinium compound by diazotization in a first synthesis vessel in the presence of mineral acid and diazotization means, said diazonium compound being next reacted, in a second synthesis step and only after having been transferred to a second synthesis vessel, into a halogenated or pseudohalogenated monomeric phenazinium compound in the presence of mineral acid and copper(I) halide or pseudohalide, the method in accordance with the invention involves a first and a second reaction step that are both run in one single vessel in the presence of the

monomeric phenazinium compound, the mineral acid, the diazotization means and the halide or pseudohalide (one pot method).

Thus, diazonium compounds are first formed using the one pot method, said
5 diazonium compounds reacting immediately *in situ* in accordance with the invention to form the halogenated or pseudohalogenated monomeric phenazinium compounds. In the event of halogenation, if the mineral acid already contains halogen, further halides need not be added.

10 The reactions are thereby preferably run using a sufficiently high concentration of halides or pseudohalides, whereby said halides or pseudohalides may be supplied in the form of salts or acids. In order to obtain pure halogenated or pseudohalogenated monomeric phenazinium compounds in good yield, the halides or pseudohalides must be utilized, depending of the type, in molar excess over the phenazinium
15 compounds. If the halides or pseudohalides are added in the form of metal halides, at least a onefold, preferably a twofold to threefold molar excess is needed. If hydrogen halides are the only halogen source used, an at least half-concentrated, preferably a concentrated acid is utilized in order to achieve a sufficiently high concentration of halide without addition of metal halides; an at least threefold molar excess over the
20 phenazinium compounds is thereby required. The diazotization means is added to the one pot method preferably last or together with the halide or pseudohalide. The reaction temperature chosen is above room temperature, and preferably ranges from 30 to 70°C, the reaction time preferably ranging from one to three hours. Usually, the reactions are run at normal pressure although it is also possible to work at a pressure
25 above atmospheric.

The monomeric phenazinium compounds which are preferably utilized as the starting compounds in the preparation method of the invention are meant to include in particular phenazinium compounds containing at least one primary amino group with
30 phenazinium compounds of the general chemical formula **VI** being particularly preferred:



wherein

- 5 R^1 , R^2 , R^4 , R^6 , R^7 , R^8 and R^9 are selected independently of each other from the group comprising hydrogen, halogen, amino, amino alkyl, hydroxy, cyano, thiocyanate, isothiocyanate, cyanate, isocyanate, mercapto, carboxy, the salt thereof, carbonic ester, sulfo, the salt thereof, sulfo ester, lower alkyl, aryl, heteroaryl and alicyclic heteroradicals,

10

R^5 is selected from a group comprising lower alkyl, aryl and heteroaryl,

A^- is an acid anion.

- 15 Particularly preferred monomeric phenazinium compounds of the general chemical formula **VI** are those belonging to the safranine dyestuffs, wherein R^1 , R^4 , R^6 and R^9 are each hydrogen, R^5 is phenyl and R^7 is $NR^{10}R^{11}$, with R^{10} and R^{11} being each independently of each other hydrogen or lower alkyl. Alkyl preferably is methyl or ethyl.

20

Aminoalkyl is meant to preferably refer to N-methylamine, N-ethylamine, N,N-dimethylamine and N,N-diethylamine. Aryl can preferably be phenyl or tolyl.

25

The acid anion A^- preferably is a sulfate, hydrogen sulfate, halide, more specifically chloride and bromide, tetrafluoroborate, hexafluorophosphate, nitrate, acetate, trifluoroacetate or methanesulfonate.

The mineral acids used in the method of the invention are preferably selected from a group comprising hydrogen halides, sulfuric acid, tetrafluoroboric acid,

hexafluorophosphoric acid, phosphoric acid and the mixtures thereof with the proviso that no hydrogen halide is used in the presence of the pseudohalides.

The preferably used diazotization means is metal nitrite, with sodium nitrite or
5 nitrosylsulfuric acid being particularly preferred.

The halides used may for example be added in the form of a hydrogen halide and/or in the form of a metal halide, meaning in the form of a salt. The metal halides used are meant to preferably include transition metal halides such as copper, nickel and
10 iron halides. According to these definitions, the following halides may for example be used: hydrochloric acid, hydrobromic acid, copper(I) chloride, copper(II) chloride, copper(I) bromide and nickel(II) chloride.

The pseudohalides used are preferably selected from a group comprising cyanate
15 ($-\text{OCN}$), thiocyanate ($-\text{SCN}$), isocyanate ($-\text{NCO}$) and isothiocyanate ($-\text{NCS}$) and can be added in the form of alkali and/or earth alkali salts.

To prepare the halogenated monomeric phenazinium compound, the monomeric phenazinium compound may for example be suspended in the mineral acid and this
20 suspension may then be heated, with stirring, to a temperature above room temperature, more specifically ranging for example from 30 to 70°C. Next, the halide, for example a metal halide dissolved in an aqueous solution, can be added. After having added the halide, the diazotization means, for example a saturated aqueous sodium nitrite solution, is added, preferably with stirring. Alternatively, the halide and
25 the diazotization means may also be added simultaneously, for example in a common solution.

In a preferred embodiment of the preparation method, the monomeric phenazinium compound can be suspended directly in a hydrogen halide, preferably at a high
30 concentration. As a result thereof, there is no need for adding further halides. This embodiment differs more specifically from the known reaction scheme for halogenating diazonium compounds according to Sandmeyer in which this reaction step normally proceeds via a radical mechanism, as also described in JP 60-056086 A, with only a catalyst such as copper powder, copper(I) or copper(II) chloride

participating in the reaction. By suspending said compound, as the only halide addition, in the respective hydrogen halide the method of the invention becomes faster, cheaper, with less impact on the environment.

- 5 In another preferred embodiment, the preparation of the halogenated monomeric phenazinium compound also advantageously departs from the Sandmeyer reaction scheme whereby here a nickel halide, for example nickel(II) chloride can be utilized instead of the known copper-type catalyst. This way of proceeding has not been described heretobefore in this context and results in significantly higher yields than
10 achieved by conventionally utilizing copper(I) chloride.

For preparing the pseudohalogenated monomeric phenazinium compound, the monomeric phenazinium compound may again be suspended preferably in the mineral acid and then heated, with stirring, to a temperature above room
15 temperature, more specifically ranging for example from 30 to 70°C. Next, the pseudohalide, for example a metal pseudohalide dissolved in an aqueous solution, may be added. After or during addition, for example in a common solution with the pseudohalide, the diazotization means, for example nitrosylsulfuric acid, may be added with stirring.

20

After the respective one of the reactions ends, the resulting halogenated or pseudohalogenated monomeric phenazinium compounds can be isolated from the reaction formulation by adding acid-neutralizing agents.

- 25 The acid-neutralizing agents preferably include earth alkali and alkali metal hydroxides, more specifically caustic soda or caustic potash lye, magnesium and calcium oxide, earth alkali and alkali metal carbonates and phosphates, more specifically sodium or magnesium carbonate or phosphate.
- 30 After the respective one of the reactions ends, the reaction formulation may also be directly regenerated by adjusting a sulfuric acid titer of < 1 wt.-% and the resulting solid matter may be filtered away.

The purity of the substances of the invention, *i.e.*, the fraction of impurities accompanying the phenazinium compounds, can be determined analytically:

To identify and quantify in accordance with the invention the compounds contained in the substances, mass spectrometry is presently more specifically utilized, whereby the spectra can be measured more specifically under the following conditions: by means of electron spray ionization coupled with a quadrupole mass spectrometer (ESI/MS) or with a quadrupole ion trap (ESI/QIT-MS), Atmospheric Pressure Matrix Assisted Laser Desorption Ionization coupled with a quadrupole ion trap (AP-MALDI/QIT-MS) or Matrix Assisted Laser Desorption Ionization coupled with a time-of-flight mass spectrometer (MALDI-TOF). The MALDI-methods are preferred. To quantitatively determine the components in the substances, the sum of all the signals in the mass spectrum is set to 100 mole-%. The height of the individual signals detected is related thereto. It is thereby assumed that ionizability and sensitivity to the assignable molecule peaks are equally high.

Alternatively, the monomeric phenazinium compounds and the oligomeric phenazinium compounds contained as impurities in the substances may also be quantitatively determined by means of another method by which a mass spectrometer is coupled with a high-performance liquid chromatography unit (LC-MS-coupling) to associate the individual peaks in the HPLC chromatogram through the mass spectrum. After a first identification from a reference mixture by means of LC-MS-coupling, the quantitative determination may then also be carried out without LC-MS-coupling by using the retention times of the peaks for identification.

Alternatively, the HPLC method can also be used for quantitatively determining the monomeric phenazinium compounds and the small amounts of additionally contained oligomeric phenazinium compounds in the substances of the invention, the gel permeation chromatography being more specifically utilized. In this case, anionic ion-pairing wetting agents can be added to the mobile phase for enhanced separation of the positively charged compounds (ion-pair chromatography).

The method of the invention permits for example to prepare compounds of high purity and having the chemical formulae **II**, **III**, **IV**, and **V** already mentioned herein above.

- 5 The preparation method of the invention will be more fully understood from the following preparation examples:

Preparation example 1: - without addition of another halide

3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride

10

1 g of 3-amino-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride was suspended in 15 ml of 35 wt.-% hydrochloric acid and heated to 50°C. Then, a saturated aqueous sodium nitrite solution (454 mg in 6 ml of water) was slowly added dropwise and was thereafter stirred for one hour at this temperature. The reaction
15 formulation was cooled down to room temperature, the resulting black-blue solid matter was filtered away and dried. The yield was 615 mg (58.5 % of the theory).

The purity of the resulting substance after quantitative analysis by means of mass spectrometry was found to be 94 mole-% i.e., 6 mole-% only of the substance utilized
20 did not consist of the monomeric compound.

Preparation example 2: - with addition of another halide

3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride

25

1 g of 3-amino-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride was suspended in 15 ml of 35 wt.-% hydrochloric acid and heated to 50°C. Then, 347 mg of nickel(II) chloride were added and a saturated aqueous sodium nitrite solution (454 mg in 6 ml of water) was slowly added dropwise and was thereafter stirred for one hour at this temperature. The reaction formulation was cooled down to room
30 temperature, the resulting black-blue solid matter was filtered away and dried. The yield was 724 mg (69.0 % of the theory).

The purity of the resulting substance after quantitative analysis by means of mass spectrometry was found to be 90 mole-% i.e., 10 mole-% only of the substance utilized did not consist of the monomeric compound.

5 Preparation example 3: - with addition of another halide

3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride

10 1 g of 3-amino-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride was suspended in 15 ml of 35 wt.-% hydrochloric acid and heated to 50°C. Then, 271 mg of copper(I) chloride were added and a saturated aqueous sodium nitrite solution (454 mg in 6 ml of water) was slowly added dropwise and was thereafter stirred for one hour at this temperature. The reaction formulation was cooled down to room temperature, the resulting black-blue solid matter was filtered away and dried. The yield was 521 mg (49.5 % of the theory).

15

The purity of the resulting substance after quantitative analysis by means of mass spectrometry was found to be 93 mole-% i.e., 7 mole-% only of the substance utilized did not consist of the monomeric compound.

20 Preparation example 4: - with addition of another halide

3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium bromide

25 1 g of 3-amino-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride was suspended in 10 ml of 48 wt.-% hydrobromic acid and heated to 50°C. Then, 392 mg of copper(I) bromide were added and a saturated aqueous sodium nitrite solution (228 mg in 2 ml of water) was slowly added dropwise and was thereafter stirred for 30 minutes at this temperature. The reaction formulation was cooled down to room temperature, the resulting black-blue solid matter was filtered away and dried. The yield was 824 mg (64.0 % of the theory).

30

The purity of the resulting substance after quantitative analysis by means of mass spectrometry was found to be even greater than 99 mole-% i.e., no impurities in the form of dimers and other oligomers could be evidenced in the substance utilized.

Preparation example 5: - without addition of another halide

3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium bromide

3 g of 3-amino-7-N,N-diethylamino-5-phenyl-phenazinium chloride were suspended
5 in 40 ml of 48 wt.-% hydrobromic acid and heated to 50°C. Then, an aqueous
concentrated sodium nitrite solution (1.094 g in 10 ml of water) was slowly added
dropwise over one hour and was thereafter stirred for another hour at this
temperature. The reaction formulation was cooled down to room temperature and
slowly incorporated in caustic soda lye. The resulting black-blue solid matter was
10 filtered away and dried. The yield was 2.571 g (67.0 % of the theory).

The purity of the resulting substance after quantitative analysis by means of mass
spectrometry was found to be approximately 89 mole-% i.e., 11 mole-% only of the
substance utilized did not consist of the monomeric compound.

15

Preparation example 6: - with addition of a pseudohalide

7-amino-2,8-dimethyl-3-thiocyanato-5-phenyl-phenazinium tetrafluoroborate

1 g of 3,7-diamino-2,8-dimethyl-5-phenyl-phenazinium chloride were suspended in
20 15 ml of 50 wt.-% tetrafluoroboric acid and heated to 50°C. Then, 10 ml of an
aqueous solution consisting of 1.109 g sodium thiocyanate and 454 mg of sodium
nitrite were added dropwise over one hour at a temperature of 50 to 60°C and
thereafter stirred for another hour at this temperature. The reaction formulation was
cooled down to room temperature, the resulting black solid matter was filtered away
25 and dried. The yield was 812 mg (64.0 % of the theory).

The purity of the resulting substance after quantitative analysis by means of mass
spectrometry was found to be approximately 90 mole-% i.e., 10 mole-% only of the
substance utilized did not consist of the monomeric compound.

30

The thus obtained halogenated and pseudohalogenated phenazinium compounds in
accordance with the present invention were added, alone or in combination with
brighteners or wetting agents, to a copper electrolyte, more specifically to an acidic,
preferably sulfuric acid bath.

To permit deposition of a copper layer onto a workpiece using an electrolytic method, said workpiece is brought, together with an anode, into contact with the bath. The bath contains copper ions and the halogenated and/or pseudohalogenated phenazinium compounds of the invention. For metal deposition, a flow of electric current is then generated between the workpiece and the anode.

The basic composition of the copper electrolyte may vary within wide limits. Generally, an acidic, copper ions containing aqueous solution of the following composition is used:

copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$)	20	–	300 g/l
preferably	180	–	220 g/l
sulfuric acid, conc.	50	–	350 g/l
preferably	50	–	90 g/l
chloride ions	0.01	–	0.25 g/l
preferably	0.05	–	0.14 g/l

Instead of the copper sulfate, it is also at least partially possible to use other copper salts. The sulfuric acid as well may be replaced in part or in whole with fluoroboric acid, methane sulfonic acid or other acids. The chloride ions are added as alkali chloride (e.g., sodium chloride) or in the form of hydrochloric acid reagent grade. The addition of sodium chloride can be dispensed with in part or in whole if the added substances already contain halide ions.

The phenazinium compounds of the present invention are preferably added to the bath in a concentration of from 0.00005 – 0.1 g/l.

The bath may moreover contain current brighteners, levellers or wetting agents. In order to obtain bright copper deposits exhibiting predetermined physical properties, at least one water-soluble sulfur compound and one oxygen-containing, high molecular compound may be added to the acidic bath of the invention. Further

additives such as nitrogen-containing sulfur compounds and/or polymeric nitrogen compounds may also be used. The oxygen-containing high molecular compounds more specifically are glycol ethers of alkyl phenols, alkanols and alkane diols, further glycol esters of aliphatic carbonic acids as well as polyethers and polyalcohols.

5

The individual components are contained in the ready-to-use bath in the following limit concentrations:

current oxygen-containing				
10	high molecular compounds	0.005	—	20 g/l
	preferably	0.01	—	5 g/l
current water-soluble organic				
	sulfur compounds	0.0005	—	0.4 g/l
15	preferably	0.001	—	0.15 g/l

Table 1 lists some of the utilizable oxygen-containing high molecular compounds.

Some sulfur compounds are set forth in Table 2. Suited functional groups are incorporated for water solubility.

20

Sulfur-containing nitrogen compounds, more specifically nitrogen-containing thio compounds, preferably thiourea derivatives and/or polymeric nitrogen compounds such as polyamines and polyamides, may be utilized in the following concentrations:

25

		0.0001	—	0.50 g/l
	preferably	0.0005	—	0.04 g/l

Preferred nitrogen-containing thio compounds are set forth in Table 3 and preferred polymeric nitrogen compounds in Table 4.

30

For preparing the bath, the individual components are added to the basic composition. The operating conditions for the bath may more specifically be adjusted as follows:

pH-value: < 1
temperature: 15°C – 50°C, preferably 20°C – 40°C
cathodic current density: 0.5 – 12 A/dm², preferably 3 – 7 A/dm²

5

The electrolyte may be agitated through a strong incident flow and possibly by injecting clean air so that the surface of the electrolyte is strongly agitated. This maximizes the mass transfer in the proximity to the electrode and allows the highest possible current densities. The movement of the cathodes also promotes mass transfer at the respective one of the surfaces. Increased convection and movement of the electrodes permit to achieve constant, diffusion-controlled deposition. The movements may be horizontal, vertical and/or caused by vibrations. In combination with air injection, they are particularly efficient.

10

15

Copper may be electrochemically replenished by dissolving copper anodes in order to keep the copper content constant. The copper used for the anodes may be a copper containing 0.02 to 0.07 wt.-% phosphorus. The copper anodes should be enclosed in a filter bag. The use of inert anodes made of platinized titanium or other coatings is also possible. Present day's prior art lines are lines in which the workpiece is coated in a vertical or horizontal position.

20

At need, filters for retaining mechanical and/or chemical residues may be inserted into the electrolyte circuits.

25

The copper electrolyte of the invention is perfectly suited for producing a decorative deposit. It may furthermore be utilized to electrolytically fill blind microvias in printed circuit boards. This constitutes a future-oriented technology for manufacturing chip carriers in particular since, in thin circuit traces, increased reliability is achieved over the technique using copper sleeves. In a similar way, the copper electrolyte of the invention provides an elegant solution to produce circuit structures onto semiconductor substrate surfaces (wafers) provided with recesses during the manufacturing of integrated circuits. Using the copper plating method of the invention, an almost constant layer thickness (planarity) is achieved over the entire

30

surface of the wafer, independent of the recesses having a high aspect ratio (1:10), so that such recesses are filled with copper.

The invention will be understood better upon reading the following method examples.

5

Method example 1 (comparative example):

In an electrolytic cell with soluble, phosphorus-containing copper anodes, a copper bath having the following composition was utilized:

10

200 g/l of copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$)

60 g/l of sulfuric acid, conc.

0.12 g/l of sodium chloride

15 The following brighteners were added:

1.5 g/l of polypropylene glycol (800 Da (dalton)),

0.006 g/l of 3-mercapto-propane-1-sulfonic acid, sodium salt

20 At an electrolyte temperature of 25°C and at a current density of 4 A/dm², a uniform, bright, slightly hazy deposit was obtained on a brushed brass sheet.

Method example 2 (comparative example):

25 4 mg/l of 7-dimethylamino-3-chloro-5-phenyl-phenazinium chloride (prepared according to the instructions given in JP 60-056086 A) were further added to the electrolyte according to method example 1. A quantitative analysis of this substance by means of mass spectrometry evidenced a fraction of impurities (more specifically of dimers and trimers of this compound) of approximately 43 mole-%.

30

After copper had been deposited under the conditions indicated in method example 1, the copper layer obtained had a slightly improved appearance. In this case, the brass sheet had a brighter appearance but showed burns (copper powder deposit) at the edges because of the high current density occurring there.

Method example 3: (example in accordance with the invention)

4 mg/l of the compound of the invention 3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride were further added to the electrolyte in accordance with method example 1.

After copper had been deposited under the conditions indicated in method example 1, the copper layer obtained on the brass sheet had a very good appearance. The deposit was mirror bright and did not show any burns. The brush lines were totally invisible now. This was indicative of an excellent leveling effect of the copper electrolyte.

Method example 4: (example in accordance with the invention)

Only 3 mg/l of the compound of the invention 7-amino-2,8-dimethyl-3-thiocyanato-5-phenyl-phenazinium-tetrafluoroborate were further added to the electrolyte in accordance with method example 1.

After copper had been deposited under the conditions indicated in example 1, the brass sheet had an extremely good appearance. The deposit was extremely brilliant and mirror-like. The sheet showed no burns. The brush lines were absolutely invisible. This was indicative of an excellent leveling effect of the copper electrolyte although the quantity of mixture had been reduced.

Result of the examples 1 through 4: it could be shown that without the halogenated or pseudohalogenated monomeric phenazinium compounds of the invention but a low leveling effect could be achieved. It could also be shown that the preparation method has a decisive influence on the quality of the halogenated and pseudohalogenated compounds used. The chlorinated compounds prepared using the method in accordance with JP 60-056086 A could not contribute to form copper layers of a satisfactory quality. The halogenated and pseudohalogenated monomeric phenazinium compounds, by contrast, have a good effect. The utilized concentration

could be clearly reduced over conventional additives with an excellent result being still achieved.

Method example 5 (comparative test):

5

To coat a printed circuit board having blind microvias, a copper bath of the following composition was utilized in an electrolytic cell having soluble, phosphorus containing copper anodes:

10 150 g/l of copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$)
 200 g/l of sulfuric acid, conc.
 0.05 g/l of sodium chloride

The following brighteners were added:

15

 0.5 g/l of polypropylene glycol (820 Da),
 0.005 g/l of bis-(ω -sulfopropyl)-disulfide, disodium salt

20 At an electrolyte temperature of 25°C and at a current density of 1 A/dm², a slightly hazy deposit was obtained on a previously 8 µm copper-reinforced printed circuit board having small blind holes (blind microvias) after an exposure time of 114 minutes, with a blind hole of a width of 110 µm and a depth of 60 µm being hardly filled with copper.

25 Method example 6: (example in accordance with the invention)

 4 mg/l of the compound of the invention, 3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium bromide, were additionally added to the electrolyte according to method example 5. After copper had been deposited under the conditions indicated in
30 method example 5, the appearance of the printed circuit board could be improved. The blind vias of a width of 110 µm and a depth of 60 µm were completely and selectively filled with copper. After copper plating had been performed, there was hardly any visible well on the copper surface. The overall quantity of deposited copper was low.

This result is a great improvement over the prior art technique known to be used for electrolytic copper plating of blind vias since these may be filled in a much better way. The reason therefore is the substantially improved leveling effect of the copper
5 plating bath obtained by the phenazinium compound of the invention. Further, the reliability of the bond between the copper deposited onto the wall of a blind via and the copper layer exposed in the hole is much better than using the conventional copper plating technique. For, using the compounds in accordance with the invention, no delaminations could be detected between the two metal layers during a
10 thermal solder shock test, whereas there is a risk that the use of known comparable additives induces such delaminations under these conditions.

It is understood that the examples and embodiments described herein are for illustrative purpose only and that various modifications and changes in light thereof
15 as well as combinations of features described in this application will be suggested to persons skilled in the art and are to be included within the spirit and purview of the described invention and within the scope of the appended claims. All publications, patents and patent applications cited herein are hereby incorporated by reference.

Table 1 : Oxygen containing high molecular compounds

Carboxy methyl cellulose
Nonyl phenol-polyglycol ether
Octane diol- <i>bis</i> -(polyalkylene glycol ether)
Octanol polyalkylene glycol ether
Oleic acid polyglycol ester
Polyethylene glycol-polypropylene glycol (block or copolymerisate)
Polyethylene glycol
Polyethylene glycol-dimethyl ether
Polypropylene glycol
Polyvinyl alcohol
β -naphthol-polyglycol ether
Stearic acid polyglycol ester
Stearyl alcohol polyglycol ether

5 Table 2: sulfur compounds

3-(benzthiazolyl-2-thio)-propyl sulfonic acid, sodium salt
3-mercapto propane-1-sulfonic acid, sodium salt
Ethylene dithio dipropyl sulfonic acid, sodium salt
Bis-(<i>p</i> -sulfophenyl)-disulfide, disodium salt
Bis-(ω -sulfoethyl)-disulfide, disodium salt
Bis-(ω -sulfo hydroxy propyl)-disulfide, disodium salt
Bis-(ω -sulfoethyl)-disulfide, disodium salt
Bis-(ω -sulfoethyl)-sulfide, disodium salt
Methyl-(ω -sulfoethyl)-disulfide, disodium salt
Methyl-(ω -sulfoethyl)-trisulfide, disodium salt
O-ethyl-dithio carbonic acid-S-(ω -sulfoethyl)-ester, potassium salt
Thioglycolic acid
Thiophosphoric acid-O-ethyl-bis-(ω -sulfoethyl)-ester, disodium salt
Thiophosphoric acid-tris-(ω -sulfoethyl)-ester, trisodium salt

Table 3: nitrogen containing thio compounds:

N-acetyl thiourea
N-trifluoroacetyl thiourea
N-ethyl thiourea
N-cyanoacetyl thiourea
N-allyl thiourea
o-tolyl thiourea
N,N'-butylene thiourea
Thiazolidine thiol(2)
4-thiazoline thiol(2)
Imidazolidine(2) (N,N'-ethylene thiourea)
4-methyl-2-pyrimidine thiol
2-thiouracil
Saccharine, sodium salt

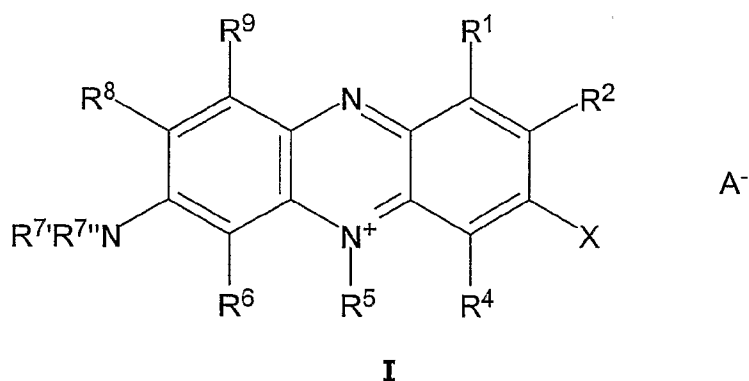
5

Table 4: polymeric nitrogen compounds

Polyethylene imine
Polyethylene imide
Polyacrylic acid amide
Polypropylene imine
Polybutylene imine
N-methyl polyethylene imine
N-acetyl polyethylene imine
N-butyl polyethylene imine

Claims:

- 5 1. Halogenated or pseudohalogenated monomeric phenazinium compounds of a purity of at least 85 mole-% having the following general chemical formula:



10 wherein

R^1 , R^2 , R^4 , R^6 , R^7 , $R^{7'}$, R^8 and R^9 are selected independently of each other from a group comprising hydrogen, halogen, amino, aminoalkyl, hydroxy, cyano, thiocyanate, isothiocyanate, cyanate, isocyanate, mercapto, carboxy, the salt thereof, carbonic acid ester, sulfo, the salt thereof, sulfoester, lower alkyl, unsubstituted aryl, substituted aryl, heteroaryl and alicyclic heteroradicals,

R^5 is selected from a group comprising lower alkyl, unsubstituted aryl, substituted aryl and heteroaryl,

X is a halogen or a pseudohalogen and

A^- is an acid anion.

- 25 2. The phenazinium compounds according to claim 1, characterized in that R^1 , R^2 , R^4 , R^6 , R^7 , $R^{7'}$, R^8 and R^9 are selected independently of each other from a group comprising hydrogen and lower alkyl.

3. The phenazinium compounds according to claim 2, characterized in that lower alkyl is methyl or ethyl.

4. The phenazinium compounds according to any one of the preceding claims,
5 characterized in that R⁵ is aryl.

5. The phenazinium compounds according to claim 4, characterized in that aryl is phenyl.

10 6. The phenazinium compounds according to any one of the preceding claims, characterized in that X is chlorine, bromine or thiocyanate.

7. The phenazinium compounds according to any one of the preceding claims,
15 characterized in that they are selected from a group comprising

- i) 3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt,
- ii) 3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt,
- iii) 3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium salt and
- iv) 7-amino-2,8-dimethyl-3-thiocyanato-5-phenyl-phenazinium salt.

20 8. The phenazinium compounds according to claim 7, characterized in that the salt is selected from a group comprising chloride, bromide, hydrogen sulfate and tetrafluoroborate.

25 9. The phenazinium compounds according to any one of claims 7 and 8, characterized in that they are selected from a group comprising

- i) 3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride,
- ii) 3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium
30 bromide,
- iii) 3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium bromide and
- iv) 7-amino-2,8-dimethyl-3-thiocyanato-5-phenyl-phenazinium
tetrafluoroborate.

10. The phenazinium compounds according to any one of the preceding claims, obtainable according to the following method:

5 a) forming a diazonium compound by diazotization of a monomeric phenazinium compound comprising at least one primary amino group in the presence of mineral acid and diazotization means in a first reaction step,

10 b) reacting the diazonium compound in a second reaction step to the halogenated or pseudohalogenated monomeric phenazinium compound in the presence of mineral acid and halide or pseudohalide,

wherein the first and the second reaction steps are both run in one single vessel.

- 15 11. A method of preparing the halogenated or pseudohalogenated monomeric phenazinium compounds in accordance with one of claims 1 – 10, comprising the following reaction steps:

20 a) forming a diazonium compound by diazotization of a monomeric phenazinium compound comprising at least one primary amino group in the presence of mineral acid and diazotization means in a first reaction step,

25 b) reacting the diazonium compound in a second reaction step to the halogenated or pseudohalogenated monomeric phenazinium compound in the presence of mineral acid and halide or pseudohalide,

characterized in that the first and the second reaction steps are both run in one single vessel.

- 30 12. The method according to claim 11, characterized in that the mineral acid is selected from a group comprising hydrogen halides, sulfuric acid, tetrafluoroboric acid, hexafluorophosphoric acid, phosphoric acid and the mixtures thereof with the proviso that no hydrogen halide is used in the preparation of the pseudohalogenated monomeric phenazinium compounds.

13. The method according to any one of claims 11 and 12, characterized in that the diazotization means is metal nitrite or nitrosylsulfuric acid.
- 5 14. The method according to claim 13, characterized in that the metal nitrite is sodium nitrite.
15. The method according to any one of claims 11 – 14, characterized in that the halide is added in the form of hydrogen halide and/or in the form of a metal
10 halide.
16. The method according to claim 15, characterized in that the metal halide is selected from a group comprising transition metal halides.
- 15 17. The method according to claim 16, characterized in that the transition metal halides are selected from a group comprising copper(I) halides, copper(II) halides, nickel(II) halides and iron(II) halides.
18. The method according to any one of claims 11 – 17, characterized in that the
20 halide is selected from a group comprising fluoride, chloride and bromide.
19. The method according to any one of claims 11 – 17, characterized in that the pseudohalide is selected from a group comprising cyanate ($-\text{OCN}$), thiocyanate ($-\text{SCN}$), isocyanate ($-\text{NCO}$) and isothiocyanate ($-\text{NCS}$).
25
20. The method according to any one of claims 11 – 19, comprising the following method steps:
- 30 i) mixing the monomeric phenazinium compounds, comprising at least one primary amino group, with the mineral acid,
ii) next heating to a temperature above room temperature,
iii) adding the halide or pseudohalide
iv) adding the diazotization means.

21. The method according to claim 20, characterized in that, in the preparation of the halogenated monomeric phenazinium compounds, the mineral acid is hydrogen halide and step iii) is eliminated.

22. The method according to any one of claims 11 – 21, characterized in that the following halogenated or pseudohalogenated monomeric phenazinium compounds are prepared:

- a) 3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride,
- b) 3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium bromide,
- c) 3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium bromide,
- d) 7-amino-2,8-dimethyl-3-thiocyanato-5-phenyl-phenazinium tetrafluoroborate.

23. An acidic bath for electrolytically depositing a copper deposit, containing at least one halogenated or pseudohalogenated monomeric phenazinium compound in accordance with any one of claims 1 – 10.

24. The bath according to claim 23, characterized in that the phenazinium compounds are contained in a concentration of from 0.00005 – 0.1 g/l.

25. The bath according to one any of claims 23 and 24, characterized in that it additionally contains compounds selected from a group comprising nitrogen-containing sulfur compounds and polymeric nitrogen compounds.

26. The bath according to claim 25, characterized in that the concentration of the nitrogen-containing sulfur compounds and the polymeric nitrogen compounds contained together in the bath is from 0.0001 – 0.50 g/l.

27. Use of the bath according to any one of claims 23 – 26 for depositing a mirror bright, leveled copper deposit for the purpose of producing decorative surfaces.

28. Use of the bath according to any one of claims 23 – 26 for forming a copper deposit on printed circuit board material.
- 5 29. Use of the bath according to any one of claims 23 – 26 for forming a copper deposit on semiconductor substrates.
- 10 30. A method of electrolytically depositing a copper deposit onto a workpiece by which the workpiece and at least one anode are contacted with the bath according to one of claims 23 – 26, and a flow of electric current is generated between the workpiece and the anodes.