CLAIMS:

1. A process for forming a copper feature over a semiconductor substrate in wafer level packaging for interconnecting an electronic circuit of a semiconductor device with a circuit external to the device, wherein the semiconductor assembly comprises a base structure bearing an under bump structure, the under bump structure comprising an under bump pad or under bump metal; the process comprising:

supplying current to an aqueous electrodeposition composition in contact with a cathode comprising the under bump structure on the semiconductor assembly, said aqueous electrodeposition composition comprising:

a) a source of copper ions,

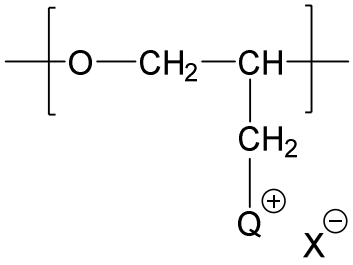
b) an acid,

c) a suppressor, and

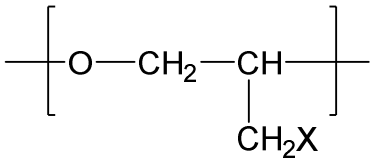
d) a leveler, wherein the leveler comprises:

(i) a quaternized dipyridyl compound, wherein the quaternized dipyridyl compound comprises a compound having a structure of a reaction product of N,N' – tetraalkylthiourea with an intermediate produced by a reaction of a dipyridyl with a difunctional alkylating agent; or

(ii) a quaternized poly(epihalohydrin), wherein poly(epihalohydrin compound comprising n rep repeating units corresponding to structure 1N and p repeating units corresponding to structure 1P:



(1N)



(1P)

wherein Q has a structure corresponding to that which may be obtained by reacting a pendent methylene halide group of poly(epihalohydrin) with a tertiary amine selected from the group consisting of: (i) $NR^aR^bR^c$ wherein each of R^a, R^b and R^c is independently selected from the group consisting of substituted or unsubstituted alkyl, alicyclic, aralkyl, substituted or

unsubstituted alkenyl, substituted or unsubstituted alkynyl, aryl and heterocyclic; (ii) an N-substituted and optionally further substituted heteroalicyclic amine wherein the N-substituent is selected from the group consisting of substituted or unsubstituted alkyl, alicyclic, aralkyl, aryl, and heterocyclic; and (iii) a substituted or unsubstituted nitrogen-containing heteroaryl compound; n is an integer between 3 and 35, p is an integer greater than 0 and up to 25; X is a halo substituent; and X^- is a monovalent anion; and

e) an accelerator;

wherein current is supplied in an electrolytic circuit comprising a direct current power source, the aqueous electrodeposition composition, the under bump pad or under bump metal in electrical communication with the negative terminal of said direct current power source and in contact with the aqueous electrodeposition composition, and an anode in electrical communication with the positive terminal of the direct current power source and in contact with said aqueous electrodeposition composition; and

wherein the current supplied in the electrolytic circuit is maintained at a current density of at least 12 A/dm^2; and

wherein a copper bump or pillar is electrodeposited on the under bump structure.

2. The process as set forth in claim 1, wherein the base structure comprises a concavity having sidewalls and a floor and the location of the under bump structure is within said concavity,

wherein lateral growth of the bump or pillar during aqueous electrodeposition is constrained by the sidewall(s) of the concavity; and

wherein the sidewalls are not conductive.

3. The process as set forth in claim 1, wherein growth of the distal end of the bump or pillar is not laterally constrained during aqueous electrodeposition.

4. The process as set forth in claim 1, wherein the under bump pad or under bump metal comprises a seminal conductive layer which functions as a cathode for initiating the aqueous electrodeposition of copper from the aqueous electrodeposition composition, and

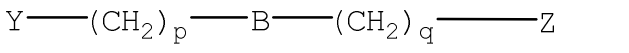
wherein the seminal conductive layer comprises a copper seed layer.

5. The process as set forth in claim 1, wherein the rate of growth of the copper bumps or pillars in the vertical direction from the under bump metal or pad is at least about 2.5 μm/min.

6. The process as set forth in claim 1, wherein the diameter of the copper bump or pillar is between about 1 and about 30 μm, and

wherein the height of the copper bump or pillar is at least about 2 μm.

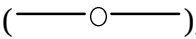
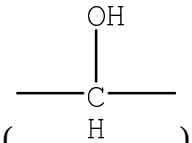
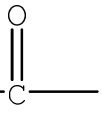
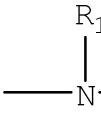
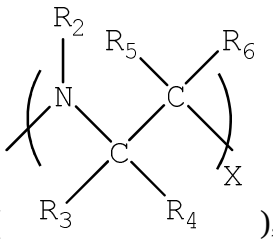
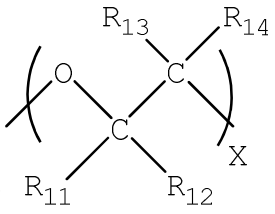
7. The process as set forth in claim 1, wherein the leveler comprises a quaternized dipyridyl compound, and wherein the difunctional alkylating agent comprises the following structure (IIIb):



Structure (IIIb)

wherein

B is selected from the group consisting of:

a single bond, an oxygen atom (), a methenyl hydroxide (), a carbonyl (), an amino (), an imino (), a sulfur atom (), a sulfoxide (), and a glycol (); and

p and q may be the same or different, are integers between 0 and 6, wherein at least one of p and q is at least 1;

X is an integer from one to four;

Y and Z are leaving groups selected from among chloride, bromide, iodide, tosyl, triflate, sulfonate, mesylate, methosulfate, fluorosulfonate, methyl tosylate, brosylate, or nosylate; and

R_1 through R_{14} are each independently hydrogen, substituted or unsubstituted alkyl having from one to six carbon atoms, substituted or unsubstituted alkylene having from one to six carbon atoms.

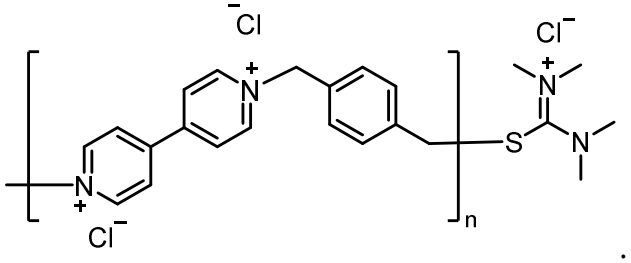
8. The process as set forth in claim 1, wherein the leveler comprises a quaternized dipyridyl compound and wherein the difunctional alkylating agent comprises the structure:

$$Y\text{-}(CR^{26}R^{27})\text{-}Ar\text{-}(CR^{28}R^{29})\text{-}Z$$

Structure A1

wherein each of Y and Z is a leaving group independently selected from among chloride, bromide, iodide, tosyl, triflate, sulfonate, mesylate, methosulfate, fluorosulfonate, methyl tosylate, brosylate, and nosylate, Ar is an bivalent aryl residue derived, e.g., from benzene, toluene, xylene, or naphthalene, and each of R26, R27, R28, and R29 is independently selected from among hydrogen and lower alkyl having 1 to 4 carbon atoms.

9. The process as set forth in claim 8, wherein the leveler comprises the general structure:



Structure D

10. The process as set forth in claim 8, wherein the leveler comprises the structure:

$$-[-(\text{di(t-amine) residue})\text{-}(CR^{26}R^{27})_i\text{-}Ar\text{-}(CR^{28}R^{29})_j\text{-}]_n\text{-}S\text{-}C(=NR^{38}R^{39})^+\text{-}NR^{40}R^{41}$$

Structure D1

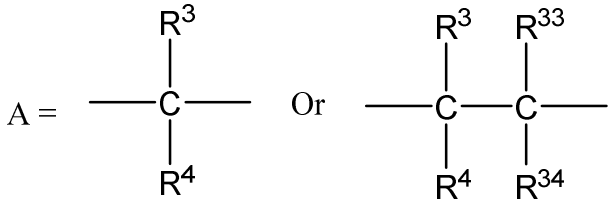
or

-[-(di-(t-amine) residue))-(CR^1R^{27})$_p$-G-(CR^5R^6)$_q$-]$_n$-S-C(=$NR^{38}R^{39}$)$^+$-$NR^{40}R^{41}$

Structure D2

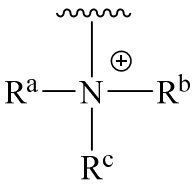
where each of R^1, R^2, R^5, R^6, R^{28}, R^{29}, R^{40} and R^{41} is independently selected from the group consisting of hydrogen and C_1 to C_4 alkyl, G is selected from the group consisting of a single covalent bond, -O-, O-(($A)_r$-O)$_s$- and -(($A)_r$-O)$_s$-

wherein A has the structure:

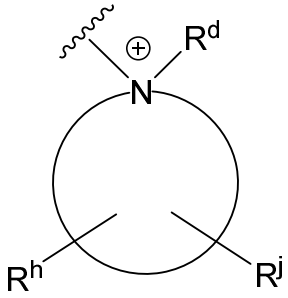


each of R^3, R^4, R^{33} and R^{34} is independently selected from the group consisting of hydrogen and C_1 to C_4 alkyl, i and j is an integer between 1 and 12, inclusive, each of p and r is an integer between 1 and 6, inclusive, s is an integer between 1 and 10, inclusive, q is an integer between 0 and 6, inclusive, and Ar is a substituted or unsubstituted arylene group.

11. The process as set forth in claim 1, wherein Q is selected from the group consisting of:

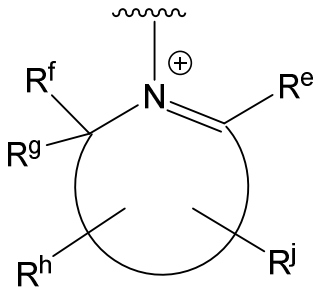


(2A)



(2B)

or



(**2C)**

wherein:

structure 2B is an N-substituted heterocyclic moiety;

structure 2C is a heterocyclic moiety;

each of R^a, R^b, R^c and R^d is independently selected from the group consisting of substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aralkyl, substituted or unsubstituted alicyclic, substituted or unsubstituted aryl, and substituted or unsubstituted heterocyclic; and

each of R^e, R^f, R^g, R^h and R^j is independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aralkyl, substituted or unsubstituted alicyclic, and substituted or unsubstituted aryl, and substituted or unsubstituted heterocyclic.

12. The process as set forth in claim 11, wherein Q corresponds to the structure that may be obtained in reacting a pendent methylene halide group of poly(epihalohydrin) with a tertiary amine that comprises $NR^aR^bR^c$, wherein one of R^a, R^b and R^c is selected from the group consisting of unsubstituted alkyl having at least three carbon atoms, hydroxyalkyl, dihydroxyalkyl, phenyl, hydroxyphenyl, dihydroxyphenyl, benzyl, hydroxyphenylmethyl and dihydroxyphenylmethyl, and each of the others of R^a, R^b and R^c is independently selected from lower alkyl having between 1 and 3 carbon atoms

13. The process as set forth in claim 11, wherein Q has the structure which may be obtained from reacting a pendent methylene chloride group of poly(epihalohydrin) with:

a) a quaternizing agent selected from the group consisting of 3-hydroxypropyldimethylamine, n-butyldimethylamine, di(3-hydroxypropyl)methylamine, 2,3-dihydroxypropyldimethylamine, 3-hydroxypropyldiethylamine, 2-hydroxypropyldimethylamine, 4-hydroxybutyldimethylamine, 2-hydroxyethyldimethylamine, n-propyldimethylamine, 2-hydroxyethoxyethyldimethylamine, di(2-hydroxyethyl)methylamine, benzyldimethylamine and 4-hydroxybenzyldimethylamine, 4-methylpyridine, 3-ethylpyridine, 4-propylpyridine, 4-tertbutylpyridine, 4-cyanopyridine, 4-isopropylpyridine, 4-methoxypyridine, 3,4-lutidine, 3-methoxypyridine, and 4-pyridinemethanol; or

b) a tertiary amine selected from the group consisting of N-methylmorpholine, 1-methylimidazole, 1-benzylimidazole, 4-ethylpyridine, 2-imidazoline, and 3-imidazoline, 2-dimethylamino-1-ethanol, 1-methylimidazole, and an N,N-dimethylalkanolamine.

14. The process as set forth in claim 11, wherein the aqueous electrodeposition composition contains between about 20 and 100 g/L copper ions, between 70 and 280 g/l of an acid selected from the group consisting of sulfuric acid and an alkane sulfonic acid, between 30 and 80 ppm chloride ions, between 1 and 50 mg/L of said leveler, and between 100 and 1000 ppm of said suppressor.

15. The process as set forth in claim 1, wherein the aqueous electrodeposition composition further comprises an accelerator, wherein the accelerator comprises an organic sulfur compound.

16. The process as set forth in claim 1, wherein the suppressor comprises a compound selected from the group consisting of:

a) an alkoxylated amine;

b) a polyether compound comprising a combination of propylene oxide (PO) repeat units and ethylene oxide (EO) repeat units present in a PO:EO ratio between 1:9 and 9:1 and bonded to a nitrogen-containing species; and

c) a polyalkylene glycol having a terminal sulfonic acid moiety and a terminal aromatic moiety formed by condensing a substituted phenol with a terminal hydroxyl of said polyalkylene glycol.

17. The process as set forth in claim 1, wherein a copper bump or pillar produced by the process has a diameter and a height, wherein an aspect ratio of the diameter and the height is at least 1:1.

18. An electrodeposition composition for depositing copper bumps or pillars on a substrate, wherein the substrate is brought into contact with the electrodeposition composition and current is supplied in an electrolytic circuit comprising the substrate as a cathode and an anode in electrical communication with a direct current power source and in contact with the electrodeposition composition comprising:

a source of copper ions;

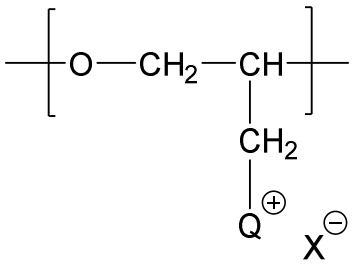
an acid;

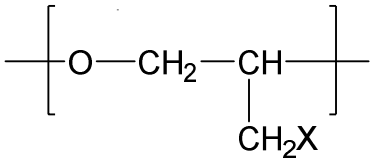
a suppressor;

a leveler, wherein the leveler comprises:

(i) a quaternized dipyridyl compound, wherein the quaternized dipyridyl compound comprises a compound having a structure of a reaction product of N,N'-tetraalkylthiourea with an intermediate produced by a reaction of a dipyridyl with a difunctional alkylating agent,or

(ii) a quaternized poly(epihalohydrin); wherein poly(epihalohydrin compound comprising n repeating units corresponding to structure 1N and p repeating units corresponding to structure 1P:





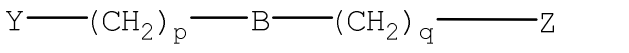
(1N) (1P)

wherein Q has a structure corresponding to that which may be obtained by reacting a pendent methylene halide group of poly(epihalohydrin) with a tertiary amine selected from the group consisting of: (i) $NR^aR^bR^c$ wherein each of R^a, R^b and R^c is independently selected from the group consisting of substituted or unsubstituted alkyl, alicyclic, aralkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, aryl and heterocyclic; (ii) an N-substituted and optionally further substituted heteroalicyclic amine wherein the N-substituent is selected from the group consisting of substituted or unsubstituted alkyl, alicyclic, aralkyl, aryl, and heterocyclic; and (iii) a substituted or unsubstituted nitrogen-containing heteroaryl compound; n is an integer between 3 and 35, p is an integer greater than 0 and up to 25; X is a halo substituent; and X^- is a monovalent anion; and

an accelerator

wherein the electrodeposition composition is configured to achieve a growth rate of the copper bumps or pillars of at least 2.5 μm/minute perpendicular to the substrate.

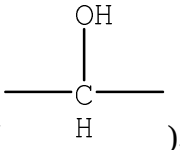
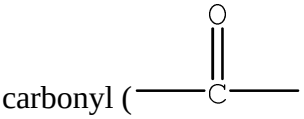
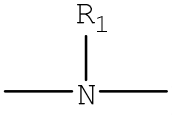
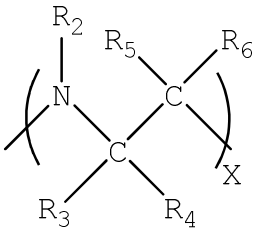
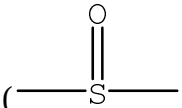
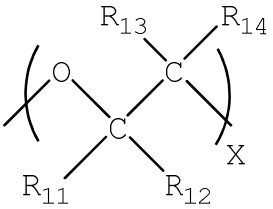
19. The electrodeposition composition as set forth in claim 18, wherein the leveler comprises a quaternized dipyridyl compound, the quaternized dipyridyl compound comprising the reaction product of dipyridyl and an alkylating agent comprising the following structure (IIIb):



Structure (IIIb)

wherein

B is selected from among:

a single bond, an oxygen atom (), a methenyl hydroxide (), a carbonyl (), an amino (), an imino (), a sulfur atom (), a sulfoxide (), and a glycol (); and

p and q may be the same or different, are integers between 0 and 6, wherein at least one of p and q is at least 1;

X is an integer from one to four;

Y and Z are leaving groups selected from among chloride, bromide, iodide, tosyl, triflate, sulfonate, mesylate, methosulfate, fluorosulfonate, methyl tosylate, brosylate, or nosylate; and

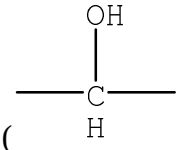
R_1 through R_{14} are each independently hydrogen, substituted or unsubstituted alkyl having from one to six carbon atoms, substituted or unsubstituted alkylene having from one to six carbon atoms, or substituted or unsubstituted aryl.

20. The composition of claim 19, wherein:

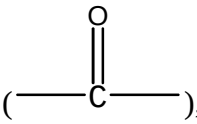
p and q are both one or are both two; and

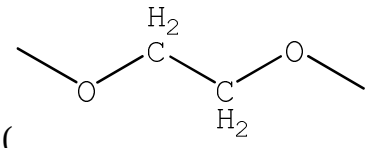
B is selected from among:

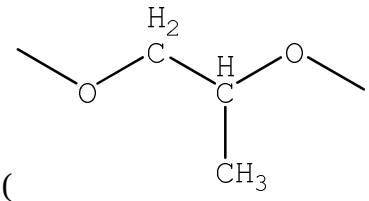
an oxygen atom (),



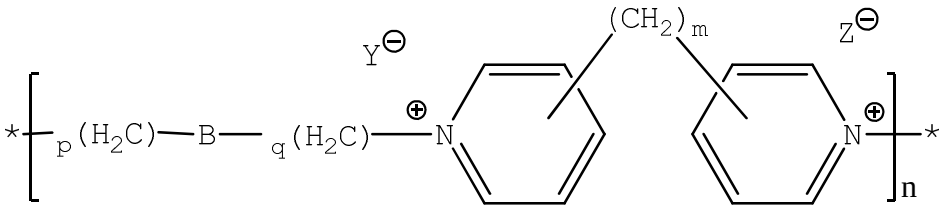
a methenyl hydroxide (),

a carbonyl (),

an ethylene glycol group (), and

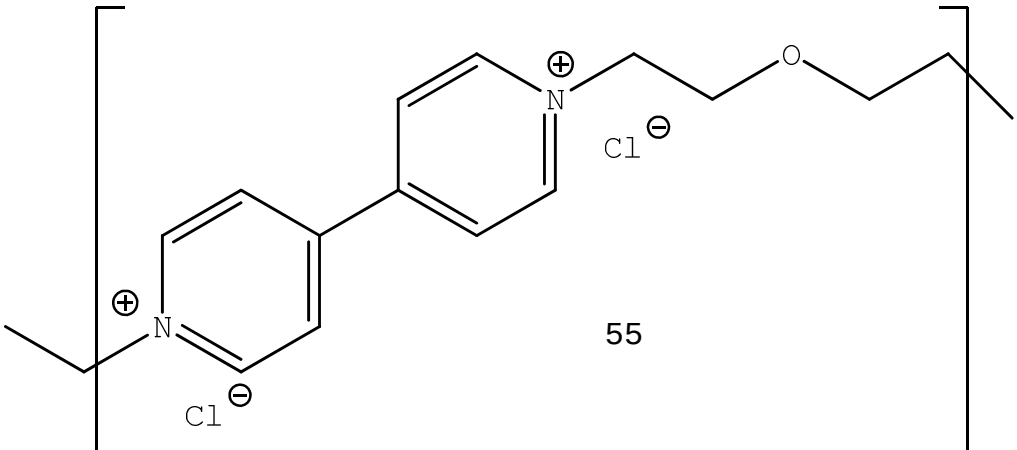
a propylene glycol group ().

21. The composition of claim 19, wherein the reaction product of the dipyridyl compound and the difunctional alkylating agent polymerizes, wherein the leveler is a polymer selected from the group consisting of the following general structures (IV), (VI), (VII), (VIII), (X), (XI), and (XXX):



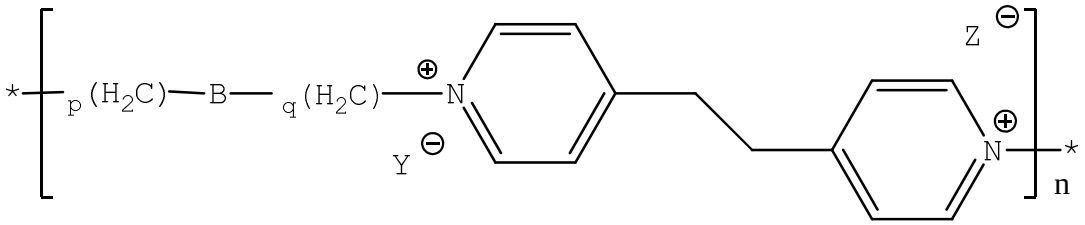
Structure (IV)

wherein B, p, q, Y, and Z are as defined with regard to (IIIb); m is an integer between one and six; and n is an integer that is at least 2;



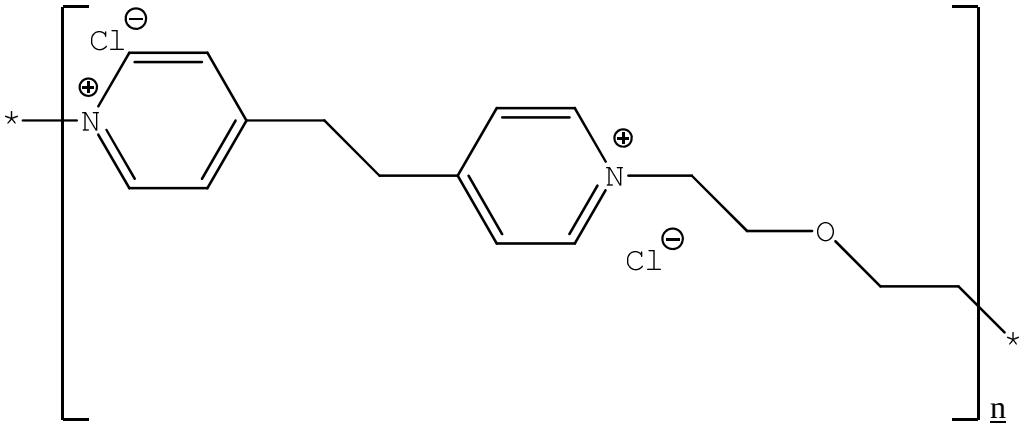
n

wherein n is an integer of at least 2;



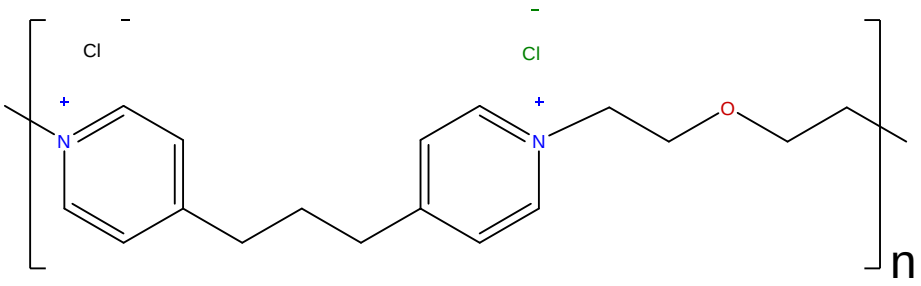
Structure (VII)

wherein B, p, q, Y, and Z are as defined with regard to structure (IIIb) and n is an integer of at least 2;



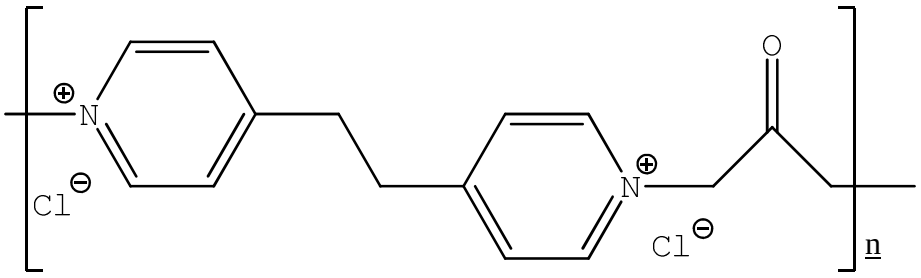
Structure (VIII)

wherein n is an integer of at least 2;



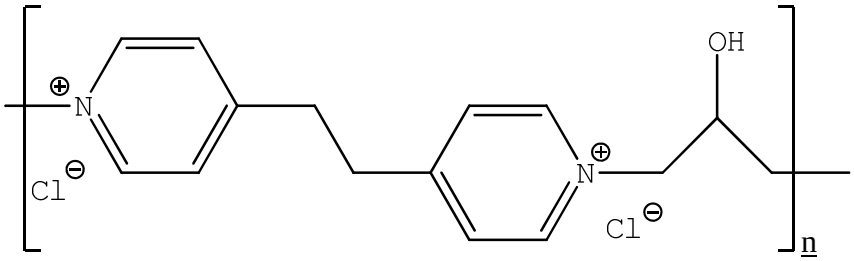
Structure (XXX)

wherein n is an integer of at least 2;



Structure (X)

wherein n is an integer of at least 2; and



Structure (XI)

wherein n is an integer of at least 2.

22. The composition as set forth in claim 19, wherein the leveler comprises a dipyridyl compound having the structure of the reaction product of N,N,N',N'-tetraalkylthiourea with an intermediate produced by reaction of a dipyridyl with a difunctional alkylating agent.

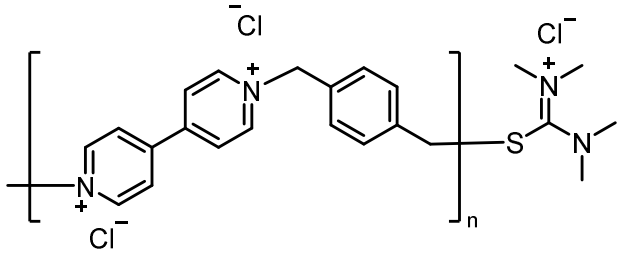
23. The composition as set forth in claim 19, wherein the difunctional alkylating agent having the structure:

$$Y\text{-}(CR^{26}R^{27})\text{-}Ar\text{-}(CR^{28}R^{29})\text{-}Z$$

Structure A1

wherein each of Y and Z is a leaving group independently selected from among chloride, bromide, iodide, tosyl, triflate, sulfonate, mesylate, methosulfate, fluorosulfonate, methyl tosylate, brosylate, and nosylate, Ar is an bivalent aryl residue derived, e.g., from benzene, toluene, xylene, naphthalene, etc., and each of R^{26}, R^{27}, R^{28}, and R^{29} is independently selected from among hydrogen and lower alkyl having 1 to 4 carbon atoms;

24. The composition as set forth in claim 19, wherein said dipyridyl compound comprises a polymer or oligomer having the general structure:



Structure D.

25. A composition as set forth in claim 19, wherein said dipyridyl compound corresponds to the formula:

$$\text{-[-(di(t-amine) residue))-}(CR^{26}R^{27})_i\text{-Ar-}(CR^{28}R^{29})_j\text{-]}_n\text{-S-C(=}NR^{38}R^{39})^{+}\text{-}NR^{40}R^{41}$$

Structure D1

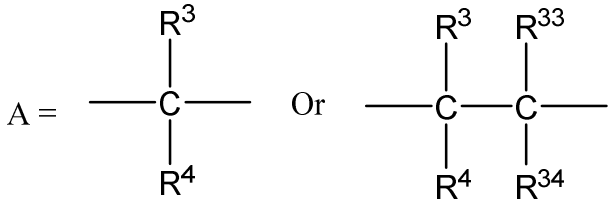
or

-[-(di-(t-amine) residue))-$(CR^1R^{27})_p$-G-$(CR^5R^6)_q$-]$_n$-S-C(=$NR^{38}R^{39}$)$^+$-$NR^{40}R^{41}$

Structure D2

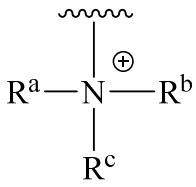
where each of R^1, R^2, R^5, R^6, R^{28}, R^{29}, R^{40} and R^{41} is independently selected from the group consisting of hydrogen and C_1 to C_4 alkyl, G is selected from the group consisting of a single covalent bond, -O-, O-$((A)_r$-$O)_s$- and -$((A)_r$-$O)_s$-

wherein A has the structure



each of of R^3, R^4, R^{33} and R^{34} is independently selected from the group consisting of hydrogen and C_1 to C_4 alkyl, i and j is an integer between 1 and 12, inclusive, each of p and r is an integer between 1 and 6, inclusive, s is an integer between 1 and 10, inclusive, q is an integer between 0 and 6, inclusive, and Ar is a substituted or unsubstituted arylene group.

26. The composition as set forth in claim 19, wherein Q is:

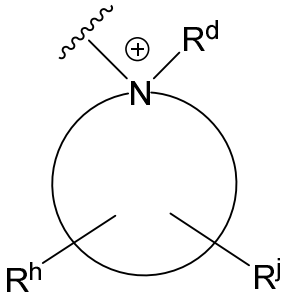


(2A)

wherein: one of R^a, R^b and R^c is selected from the group consisting of hydroxyalkyl, dihydroxyalkyl, phenyl, hydroxyphenyl, dihydroxyphenyl, benzyl, hydroxyphenylmethyl, and

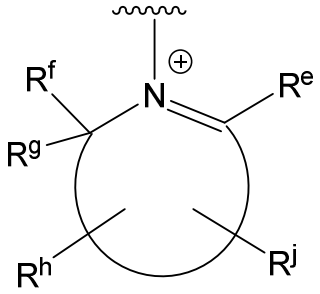
dihydroxyphenylmethyl, and each of the others of R^a, R^b and R^c is independently selected from lower alkyl having between 1 and 3 carbon atoms; or

wherein Q is



(2B)

or



(**2C**)

wherein:

structure 2B is an N-substituted heterocyclic moiety;

structure 2C is a heterocyclic moiety; each of R^e, R^f, R^g, R^h and R^j is independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aralkyl, substituted or unsubstituted alicyclic, and substituted or unsubstituted aryl, and substituted or unsubstituted heterocyclic;

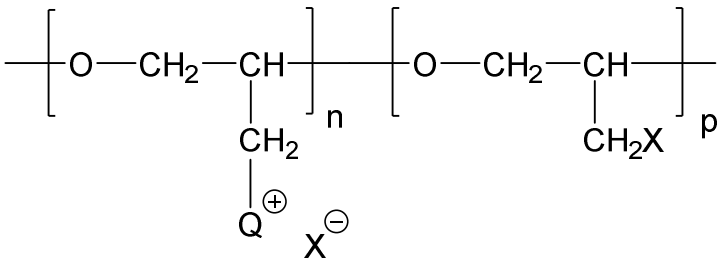
n is an integer between 3 and 35;

p is an integer greater than 0 and up to 25;

X is a halo substituent; and

X is a monovalent anion.

27. The composition as set forth in claim 26, wherein repeating units of said poly(epihalohydrin) consist essentially of residues of epihalohydrin and residues of quaternized epihalohydrin



(I)

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28. The composition as set forth in claim 26, wherein Q corresponds to the structure that may be obtained in reacting a pendent methylene halide group of poly(epihalohydrin) with a tertiary amine that comprises $NR^aR^bR^c$, wherein one of R^a, R^b and R^c is selected from the group consisting of unsubstituted alkyl having at least three carbon atoms, hydroxyalkyl, dihydroxyalkyl, phenyl, hydroxyphenyl, dihydroxyphenyl, benzyl, hydroxyphenylmethyl and dihydroxyphenylmethyl, and each of the others of R^a, R^b and R^c is independently selected from lower alkyl having between 1 and 3 carbon atoms.

29. The composition as set forth in claim 26, wherein Q has the structure which may be obtained from reacting a pendent methylene chloride group of poly(epihalohydrin) with:

a) a quaternizing agent selected from the group consisting of 3-hydroxypropyldimethylamine, n-butyldimethylamine, di(3-hydroxypropyl)methylamine, 2,3-dihydroxypropyldimethylamine, 3-hydroxypropyldiethylamine, 2-hydroxypropyldimethylamine, 4-hydroxybutyldimethylamine, 2-hydroxyethyldimethylamine, n-propyldimethylamine, 2-

hydroxyethoxyethyldimethylamine, di(2-hydroxyethyl)methylamine, benzyldimethylamine and 4-hydroxybenzyldimethylamine; or

b) a pendent methylene halide group with a tertiary amine selected from the group consisting of 3-hydroxypropyldimethylamine, n-butyldimethylamine, di(3-hydroxypropyl)methylamine, 2,3-dihydroxypropyldimethylamine, 3-hydroxypropyldiethylamine, 2-hydroxypropyldimethylamine, 4-hydroxybutyldimethylamine, 2-hydroxyethyldimethylamine, n-propyldimethylamine, 2-hydroxyethoxyethyldimethylamine, di(2-hydroxyethyl)methylamine, benzyldimethylamine, and 4-hydroxybenzyldimethyleamine, 4-methylpyridine, 3-ethylpyridine, 4-propylpyridine, 4-tertbutylpyridine, 4-cyanopyridine, 4-isopropylpyridine, 4-methoxypyridine, 3,4-lutidine, 3-methoxypyridine, and 4-pyridinemethanol.

30. The composition as set forth in claim 26, wherein the aqueous electrodeposition composition further comprises an accelerator, wherein the accelerator comprises an organic sulfur compound.

31. The composition as set forth in claim 18, wherein the suppressor comprises a compound selected from the group consisting of:

a) an alkoxylated amine;

b) a polyether compound comprising a combination of propylene oxide (PO) repeat units and ethylene oxide (EO) repeat units present in a PO:EO ratio between 1:9 and 9:1 and bonded to a nitrogen-containing species; and

c) a polyalkylene glycol having a terminal sulfonic acid moiety and a terminal aromatic moiety formed by condensing a substituted phenol with a terminal hydroxyl of said polyalkylene glycol.