United States Patent

Passal et al.

[15] **3,678,055**

[45] **July 18, 1972**

[54] N-2,3-DIBROMOPROPENYL PYRIDINIUM, QUINOLINIUM AND ISOQUINOLINIUM DERIVATIVES

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[73] Assignee: **M & T Chemicals Inc.**, New York, N.Y.

[22] Filed: **June 12, 1969**

[21] Appl. No.: **870,954**

Related U.S. Application Data

[62] Division of Ser. No. 387,799, Aug. 5, 1964, abandoned.

[52] **U.S. Cl.** .....**260/290 R,** 260/283 R, 260/283 S, 260/283 CN, 260/288 R, 260/287 R, 260/289 R, 260/294.8 F, 260/294.9, 260/295 R, 260/295 Q, 260/295.5, 260/296 R, 260/297 R, 260/288 R, 204/49

[51] **Int. Cl.** **C07d 31/26,** C07d 33/36

[58] **Field of Search**.....260/290, 294.9, 296, 297, 283, 260/289, 288, 287

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

This invention is directed to N-2,3-dibromopropenyl pyridinium salts which find use in nickel electroplating baths and processes.

The present invention relates to novel compositions of matter and to improved nickel electroplating baths and processes.

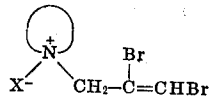
7 Claims, No Drawings

N-2,3-DIBROMOPROPENYL PYRIDINIUM, QUINOLINIUM AND ISOQUINOLINIUM DERIVATIVES

This application is a divisional application of Ser. No. 387,799, filed Aug. 5, 1964, now abandoned.

It is an object of this invention to provide novel compositions of matter. Another object of this invention is to provide a process for producing novel compositions of matter. Still another object of this invention is to provide superior baths for electrodepositing bright and smooth nickel. Another object of this invention is to provide superior processes for electrodepositing bright and smooth nickel. Other objects will be apparent to those skilled in the art on inspection of the following description.

The novel products of this invention according to certain of its aspects comprise N-2,3-dibromopropenyl pyridinium, quinolinium and isoquinolinium salts which may have the general formula



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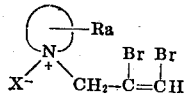


may be pyridine, quinoline or isoquinoline; and X may be a bath-soluble, bath-compatible anion.

The novel compounds of this invention contain the group



which may be pyridine, quinoline or isoquinaline. In accordance with certain more specific aspects of this invention the preferred salts may have the formula



wherein

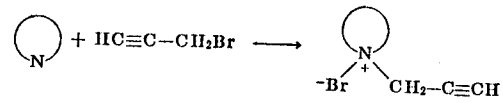


is selected from the group consisting of pyridine, quinoline, and isoquinoline; X is a bath-compatible, bath-soluble anion; *a* is 0–3; and R is an inert substituent selected from the group consisting of alkyl having one to four carbon atoms, hydroxyalkyl having one to four carbon atoms, halogen, alkoxy, carboxyl, carbalkoxy, acetyl, benzyl, sulfo, carboxamido, and cyano. Inert substituents are substituents which do not undesirably react with other components of the plating baths, interfere with the preparation of the novel compounds or render them insoluble in the plating bath. Typical inert substituents which may be present include alkyl; halogens; hydroxyalkyl; cyano; alkoxy; carboxyl; carbalkoxy; acetyl; benzyl; sulfo; carboxamido; etc, or combinations thereof. It is preferred that a maximum of three inert substituents be present. If there be more than one substituent, they may be the same or different. Where the substituent contains alkyl it may preferably contain one to four carbon atoms and most preferably it may be methyl.

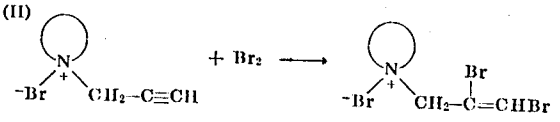
For the sake of convenience, the following description will be directed to the pyridine embodiment. It is to be understood, however, that the description is equally applicable to the quinoline and isoquinoline embodiments and to the substituted reactants as described above.

These novel salts may be prepared by reacting together pyridine and propargyl bromide to give N-2-propynyl pyridinium bromide (which may also be designated N-propargyl pyridinium bromide), and brominating the N-2-propynyl pyridinium bromide to N-2,3-dibromopropen-2-yl pyridinium bromide (which may also be designated N-2,3-dibromoallyl pyridinium bromide). These two steps may be represented as

(I)



(II)



The pyridine reactant employed may incle pyridine se; 2-methylpyridine; 3-methylpyridine; 4-methylpyridine; 2-ethylpyridine; 4-n-butylpyridine; 3,5-dimethylpyridine; 3,4-dimethylpyridine; 2-benzylpyridine; 3-benzylpyridine; 3-bromopyridine; 4-chloropyridine; 3,5-dibromopyridine; 3-ethyl-4-methypyridine; 4-isopropylpyridine; 4-methoxypyridine; 2,4,6-trimethylpyridine; 3-pyridinecarboxylic acid; 3,5-pyridinedicarboxylic acid; 3-pyridinesulfonic acid; 3-pyridinecarboxamide (nicotinamide); 2-amino-6-methylpyridine; The quinoline or isoquinoline reactant employed may include quinoline; 3-chloroquinoline; 2-methylquinoline; 4-methylquinoline; 8-methylquinoline; 2,6-dimethylquinoline; isoquinoline; etc.

The reaction between the pyridine compound and the propargyl bromide may be effected by mixing them together, preferably in the presence of a liquid inert diluent or solvent, e.g. dimethylformamide. The reaction may be carried out over a range of temperatures, typically −10° C. to 40° C. and preferably about 0°–30° C. Good yield of N-propynyl pyridinium bromide may be obtained when substantially stoichiometric, i.e. equimolar quantities of the two reactants are employed, but excess of either reactant may be employed if desired.

The product from reaction (I) may then be brominated according to reaction (II) to produce the desired N-2,3-dibromopropenyl pyridinium bromide. Bromination may be done in the same solvent in which the N-propynyl pyridinium halide was prepared or the quaternary salt may be isolated and re-dissolved in a second inert solvent prior to halogenation. Water may be a preferred solvent for the halogenation reaction.

The N-propynyl pyridinium bromide may preferably be brominated by contacting it with bromine, se, or with an equivalent halogenating agent. Bromine may be added to the reaction vessel or formed in situ. e.g. by reaction of potassium bromate and potassium bromide in acid solution. Halogenating catalysts including metal salts, peroxides, light, etc. may be employed, although the reaction may typically be rapid and essentially quantitative in the absence of catalysts. Preferably, stoichiometric quantities of the reactants may be employed.

The brominating agent may preferably be added to the solution of N-propynyl pyridinium halide and the resultant mixture heated, typically to about 50°–120° C. and preferably to about 90°–110° C. The reaction may be substantially complete in a short time, typically 1 hour or less, as evidenced by disappearance of the bromine. Product N-2,3-dibromopropenyl pyridinium bromide may be isolated by stripping off the solvent, preferably on a steam bath. The product may be further purified e.g. by recrystallization.

The N-2,3-dibromopropenyl pyridinium bromides may be employed as such or the labile halide anion may be replaced by other anions to produce other novel compounds. For example, the bromide anion formed on dissolving the quaternary chloride salt in aqueous solution may be replaced by other

soluble, bath-compatible anions hereinafter designated as X^-_n. A soluble, bath-compatible anion may be an anion which in combination with the novel compound renders the latter soluble in aqueous nickel electroplating baths in amount sufficient to give a primary brightening effect; and which is compatible with the compounds of the bath i.e. which does not interfere with satisfactory operation of the bath. Typical anions may include bromide, chloride, iodide, fluoride, acetate, sulfate, methosulfate, ethosulfate, citrate, and chloroacetate. Preferred anions may include halide, i.e. fluoride, chloride, and iodide, and perchlorate. For example, a pyridinium acetate salt may be prepared by reacting the pyridinium bromide quaternary salt with silver acetate. Iodide may be substituted for bromide by reacting the pyridinium bromide salt in aqueous solution with e.g. sodium iodide in ethanol, etc.

Illustrative of the preparation of the salts of the present invention are the following examples:

EXAMPLE 1

To a solution of 36 g. of propargyl bromide (0.3 mole) in 25 ml. dimethylformamide at 0° C. there was added 20 g. of pyridine (0.25 mole). The mixture was chilled overnight to give a clear, slightly red solution. This was allowed to warm to room temperature and was poured into 500 ml. of acetone to give a light tan oil which solidified on stirring. The product was filtered, washed with acetone and dried in a vacuum dessicator over phosphorus pentoxide. The yield of product N-propynyl pyridinium bromide was 37 g. (74 percent), melting point 115°–116° C.

EXAMPLE 2

10 g. of the product of Example 1 (0.05 mole) was dissolved in 100 ml of water and 8 g. (0.05 mole) of bromine was added thereto. An orange precipitate was formed. The mixture was heated to reflux and the orange precipitate turned to a dark red oil which dissolved completely after stirring for 30 minutes at reflux. The water was evaporated off on a steam bath with a stream of air and the light tan solid which was formed was dissolved in isopropanol, decolorized with activated charcoal and recrystallized from isopropanol after filtration to give 15 g. (83 percent) of N-2,3-dibromopropenyl pyridinium bromide having a melting point of 146°–147° C. and containing 22.0 percent ionizable bromine (22.4 percent theory).

EXAMPLE 3

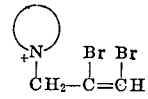
10 g. of 2,4,6-trimethylpyridine, 20 ml of propargyl bromide, and 25 ml of dimethylformamide were mixed together and allowed to stand for 30 hours at room temperature. 25 ml of acetone was added and the mixture allowed to stand an additional 5 days, after which the crystalline precipitate which was formed was filtered off, washed with acetone, and air dried to give 14.1 g. (70 percent) of N-propynyl 2,4,6-trimethylpyridinium bromide having a melting point of 198°–199° C. and containing 33.5 percent ionizable bromine (theory 33.2 percent).

12 g. (0.05 mole) of this product was dissolved in 100 ml of water and 8 g (0.05 mole) of bromine was added thereto. An orange precipitate was formed immediately. The mixture was slowly heated to reflux and refluxing was continued until the precipitate dissolved and the orange color disappeared. The solution was evaporated to dryness on a steam bath. The salt residue was triturated with acetone and filtered. After recrystallization from dimethylformamide and acetone there was obtained 15 g. of N-2,3-dibromopropenyl 2,4,6-trimethylpyridinium bromide having a melting point of 181°–183° C. and containing 19.9 percent ionizable bromine (theory 19.9 percent).

EXAMPLE 4

2 g. of N-propynyl quinolinium bromide was dissolved in 25 ml of water and there was added thereto a solution of 0.5 g. $KBrO_3$ and 1.7 g. of KBr in 25 ml. of water. To this solution there was added 2 ml of a 1:1 by volume solution of concentrated sulfuric acid in water. A voluminous lemon yellow precipitate was formed immediately. The mixture was slowly heated to reflux and refluxed for 30 minutes, after which a very small amount of undissolved material was present. The solution of product N-2,3-dibromopropenyl quinolinium bromide was treated with activated carbon, filtered, and diluted to a volume of 250 ml.

In accordance with certain of its aspects, this invention may comprise the process for electro-depositing nickel from an aqueous nickel electroplating bath containing 1 g/l – 20 g/l of a secondary brightener typically a secondary brightener selected from the group consisting a saccharin, dibenzene sulfonamide, o-benzene sulfonamide, sodium benzene monosulfonate, 1,3,6-naphthalene trisulfonate, o-sulfobenzaldehyde, and sulfonated dibenzothiophene dioxide (prepared by reacting diphenyl with fuming sulfuric acid and isolating and neutralizing the resultant product) and 0.005 g/l – 0.1 g/l of a primary brightener containing a cation having the structure

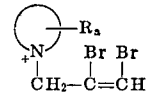


wherein



has the definition hereinbefore stated.

According to certain preferred aspects of this invention, the cation may have the formula



wherein



R, and a have the definitions given supra.

The novel compounds when used as primary brighteners may be present preferably in amounts of about 0.005 g/l – 0.1 g/l, preferably 0.01 g/l – 0.05 g/l.

The basis metal on which the metal may be electrodeposited in accordance with this invention may preferably be copper or copper alloys; ferrous metals including sheet iron; or other metals including nickel, etc.

Addition agents as brighteners in bright nickel plating baths may be divided, broadly, into two classes on the basis of their function. Secondary brighteners (1) may increase the brightness of an ordinarily dull or matte deposit but not to a full or mirror bright stage and (2) may impart a ductilizing effect. The use of primary brighteners in conjunction with secondary brighteners may result in mirror bright deposits. It is preferred to use with the novel primary brighteners of this invention an auxiliary secondary brightener to provide superior deposit luster. These auxiliary secondary brighteners may preferably be unsaturated hydrocarbon sulfonates including sodium 2-propene-1 sulfonate; sodium 3-chloro-2-butene sulfonate; the mixed isomers of sodium 3-butene-2-hydroxy-1-sulfonate and sodium 3-butene-1-hydroxy-2-sulfonate; sodium 2-propyne-1-sulfonate; and sodium 1-phenylethene-2-sulfonate.

The preferred pyridinium, quinolinium and isoquinolinium salts of the present invention are particularly potent and extremely effective brighteners. The particular preferred concentration of the salt used in a given bath may depend on the

secondary brightener used, the auxiliary secondary brightener, and such other factors as the degree of luster, and rate of brightening and leveling desired, and the finish of the basis metal. The preferred secondary brighteners may be generally characterized by the presence of at least one sulfone or sulfonic acid group attached to a nuclear carbon of an aromatic hydrocarbon ring e.g. benzene, naphthalene, etc. They may be used in amounts of 1 g/l – 75 g/l, and preferably 1 g/l – 20 g/l. The preferred secondary brighteners, which may contain a sulfonate or sulfone bonded to an aromatic structure, may include saccharin, dibenzenesulfonamide, and sodium benzene monosulfonate.

The primary brighteners of the present invention may be useful with e.g. Watts Type Baths and High Chloride Type Baths, including those typified by the illustrative baths of Tables I and II.

TABLE I

Watts-Type Baths

nickel sulfate	200 to 400 g/l
nickel chloride	30 to 75 g/l
boric acid	30 to 50 g/l
temperature	30° C. to 65° C.
pH	3.5 to 5.0 electrometric
with agitation (either mechanical, air, or solution circulation by pumping)	

TABLE II

High Chloride Baths

nickel chloride	150 to 300 g/l
nickel sulfate	40 to 150 g/l
boric acid	30 to 50 g/l
temperature	30° C. to 65° C.
pH	3.5 to 5.0 electrometric
with agitation (either mechanical, air, or solution circulation by pumping)	

Other nickel plating baths include those containing, as a source of nickel, nickel fluoborate with nickel chloride, nickel sulfamate with nickel chloride, etc.

The plating conditions for electrodeposition from the aforementioned baths may for example include temperature of 40° C. – 70° C, pH of 3.5–5 electrometric, and preferably 3.8–4.5, cathode current density of 1–10 amps. per sq. dm. Typical preferred current density of the baths of Table I may be 4–6 amps. per sq. dm. Agitation may be preferred while plating.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given.

In Examples 5–34 a Watts-Type Bath having 300 g/l of nickel sulfate, 60 g/l of nickel chloride, and 45 g/l of boric acid and having an electrometric pH of 4.0 was used. In Examples 5–16, sodium dihexylsulfosuccinate was used as the wetting agent with air agitation. In the remaining Examples, sodium lauryl sulfate was used, with mechanical agitation. The amount of wetting agent used was: 0.01 g/l in Examples 6, 7, 17–22 and 24; 0.1 g/l in Examples 13 and 26; 0.2 g/l in Examples 11 and 28; and 0.25 g/l in the remaining Examples. Brilliant, mirror bright, highly leveled electrodeposits were obtained in all the tests.

In Examples 5–34, the primary brighteners are identified in accordance with the following code:

Primary Brightener Compound	
A	N-2,3-dibromopropenyl 2,4,6-trimethylpyridinium bromide
B	N-2,3-dibromopropenyl 3,5-dimethylpyridinium bromide
C	N-2,3-dibromopropenyl 4--isopropylpyridinium bromide
D	N-2,3-dibromopropenyl 2,6-dimethylpyridinium bromide
E	N-2,3-dibromopropenyl 2-aminopridinium bromide
F	N-2,3-dibromopropenyl 3-methylpyridinium bromide
G	N-2,3-dibromopropenyl 3-cyanopyridinium bromide
H	N-2,3-dibromopropenyl 4-ethylpyridinium bromide
I	N-2,3-dibromopropenyl 4-methylpyridinium bromide
J	N-2,3-dibromopropenyl 2,4-dimethylpyridinium bromide
K	N-2,3-dibromopropenyl 2-chloropyridinium bromide
L	N-2,3-dibromopropenyl 2-ethylpyridinium bromide
M	N-2,3-dibromopropenyl 2-beta-hydroxyethyl pyridinium bromide
N	N-2,3-dibromopropenyl 2-γ-hydroxypropyl-pyridinium bromide
O	N-2,3-dibromopropenyl 2-methylquinolinium bromide
P	N-2,3-dibromopropenyl 2-p-methoxybenzylamino-pyridinium bromide
Q	N-2,3-dibromopropenyl isoquinolinium bromide
R	N-2,3-dibromopropenyl 3-sulfopyridinium bromide (Na Salt)
S	N-2,3-dibromopropenyl 3-hydroxymethylpyridinium bromide
T	N-2,3-dibromopropenyl 2-Methylpyridinium bromide
U	N-2,3-dibromopropenyl 3,4-dimethylpyridinium bromide
V	N-2,3-dibromopropenyl 2,5-dimethylpyridinium bromide
W	N-2,3-dibromopropenyl 3-ethyl-4-methylpyridinium bromide
X	N-2,3-dibromopropenyl 4-methylquinolinium bromide
Y	N-2,3-dibromopropenyl 2-aldoximopyridinium bromide
Z	N-2,3-dibromopropenyl 2,6-diaminopyridinium bromide

Ex. No.	Additives	Amt. g/l	c.d., a/dm	Temp. °C.
5	Primary Brightener A	0.02	4.0	60
	saccharin	2		
	sodium 3-chloro-2-butene sulfonate	3		
6	Primary Brightener D	0.02	4.0	60
	saccharin	2		
	sodium 3-chloro-2-butene sulfonate	3		
7	Primary Brightener W	0.02	4	60
	saccharin	3		
	sodium 3-chloro-2-butene sulfonate	3		
8	Primary Brightener A	0.03	3	55
	dibenzene sulfonamide	3		
	sodium 2-propene-1-sulfonate	2		
9	Primary Brightener A	0.03	5	55
	N,N'-bis (phenyl-sulphonyl) 4,4'-diphenyl disulfonamide	3		
	sodium 2-propene-1-sulfonate	2		
10	Primary Brightener A	0.03	5	55
	sulfonated dibenzothiophene dioxide	4		
	sodium 2-propene-1-sulfonate	2		
11	Primary Brightener V	0.04	5	60
	dibenzene sulfonamide	4		
	sodium 2-propene-1 -sulfonate	2		
12	Primary Brightener V	0.04	5	60
	dibenzene sulfonamide	4		
	sodium 3-chloro-2-butene sulfonate	3		
13	Primary Brightener A	0.03	6	60
	saccharin	2		
	sodium 3-chloro-2-butene sulfonate	3		
14	Primary Brightener N	0.02	6	60
	dibenzene sulfonamide	3		
	sodium 3-chloro-2-butene sulfonate	2		
15	Primary Brightener N	0.03	6	60
	N,N'-bis (phenyl-sulfonyl) 4,4'-diphenyl disulfonamide	4		
	sodium 2-propene-1-sulfonate	2		

16	Primary Brightener N sulfonated dibenzothiophene dioxide sodium 2-propene-1-sulfonate	0.03 4 2	6	60
17	Primary Brightener G saccharin sodium 3-chloro-2-butene sulfonate	0.02 2 3	4	60
18	Primary Brightener J saccharin sodium 3-chloro-2-butene sulfonate	0.02 2 3	4	60
19	Primary Brightener M saccharin sodium 3-chloro-2-butene sulfonate	0.03 2 3	4	60
20	Primary Brightener O saccharin sodium 3-chloro-2-butene sulfonate	0.02 2 3	4	60
21	Primary Brightener P saccharin sodium 3-chloro-2-butene sulfonate	0.03 2 3	4	60
22	Primary Brightener Q saccharin sodium 3-chloro-2-butene sulfonate	0.04 2 4	4	60
23	Primary Brightener V saccharin sodium 3-chloro-2-butene sulfonate	0.03 3 3	4	60
24	Primary Brightener Z saccharin sodium 3-chloro-2-butene sulfonate	0.02 2 3	4	60
25	Primary Brightener A dibenzene sulfonamide sodium 3-chloro-2-butene sulfonate	0.03 3 2	5	55
26	Primary Brightener V saccharin sodium 2-propene-1-sulfonate	0.03 2 2	5	60
27	Primary Brightener V saccharin sodium 2-propene-1-sulfonate	0.03 2 2	5	60
28	Primary Brightener V saccharin sodium 2-propene-1-sulfonate	0.03 3 2	5	60
29	Primary Brightener A saccharin sodium 3-chloro-2-butene sulfonate	0.02 2 3	6	60
30	Primary Brightener A dibenzene sulfonamide sodium 2-propene-1-sulfonate	0.03 4 2	6	60
31	Primary Brightener V dibenzene sulfonamide sodium 3-chloro-2-butene sulfonate	0.03 4 2	6	60
32	Primary Brightener V sulfonated dibenzothiophene dioxide sodium 3-chloro-2-butene sulfonate	0.03 4 2	6	60
33	Primary Brightener V saccharin sodium 2-propene-1-sulfonate	0.03 2 3	6	60
34	Primary Brightener V saccharin sodium 3-chloro-2-butene sulfonate	0.02 2 2	6	60

The foregoing examples illustrate specific baths and processes, which permit attainment of mirror bright, highly leveled nickel deposits. Substantially similar results are obtained when other compounds of this invention as hereinbefore described are employed.

The nickel electrodeposits obtained from baths utilizing the novel brightener combination are advantageous in that mirror bright lustrous electrodeposits having a high degree of ductility may be obtained over a wide range of current densities.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

What is claimed is:

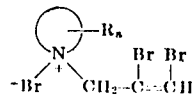
1. N-2,3-dibromopropenyl 3-cyanopyridinium bromide.

2. N-2,3-dibromopropenyl 2-p-methoxybenzylamino pyridinium bromide.

3. N-2,3-dibromopropenyl 2,6-diaminopyridinium bromide.

4. N-2,3-dibromopropenyl 2-amino-6-methylpyridinium bromide.

5. The process for preparing a member selected from the group consisting of N-2,3-dibromopropenyl pyridinium bromide and N-2,3-dibromopropenyl quinolinium bromide having the formula



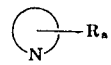
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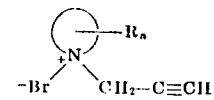
selected from the group consisting of pyridine, quinoline and isoquinoline; *a* is 0–3 and when



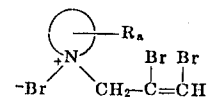
is isoquinoline, *a* is 0; and R is a substituent selected from the group consisting of alkyl having one to four carbon atoms, hydroxyalkyl having one to four carbon atoms, halogen, methoxy, carboxyl, amino benzyl, sulfo, carboxamide, and cyano which comprises mixing together at about −10 to 40° C.



and propargyl bromide in the presence of an inert diluent thereby forming a compound of the formula



and contacting said compound with bromine in the presence of water as inert diluent thereby forming the product



6. The process claimed in claim 5 wherein said bromine and said compound are contacted in stoichiometric quantities.

7. The process claimed in claim 5 wherein said



and said propargyl bromide are mixed together in substantially equimolar quantities.

* * * * *