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Index at acceptance—39N[III], 70C5+6[LVIII(5)]

PROVISIONAL SPECIFICATION

AN ELECTROLYTIC PROCESS FOR THE PREPARATION OF COPPER OXYCHLORIDE

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG. NEW DELHI, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860)

The following specification particularly describes the nature of this invention :—

This is an invention by Srinivasa Sampath, Ramaswamy Thangappan Nadar and Subramaniam Ramajayam, all of Central Electrochemical Research Institute, Karaikudi-3 (Madras State), India, all Indians.

This invention relates to an electrolytic process for the preparation of copper oxychloride, which can be used as fungicide, pigment, wood preservative etc.

Hitherto, it has been proposed to make copper oxychloride by chemical methods wherein copper is reacted with hydrochloric acid in the presence of air or a copper salt like cuprous chloride or copper sulphate is reacted with other suitable chemicals to yield the copper oxychloride. In the electrochemical method, the formation of copper oxychloride is reported by the electrolysis of sodium chloride solution at a very high current density at copper anode, or low current density and bubbling air. Copper oxychloride is also said to be formed by the electrolysis of a mixed electrolyte containing sodium chloride and sulphate at copper anode in conjunction with an auxiliary graphite anode.

This is open to the objection that the copper oxychloride formed varies widely in the contents of copper and chlorine (chloride 7 to 31% and copper 52 to 68% depending on the reactants and conditions of reaction; the method of preparation (particularly the chemical method) involves a number of steps and the rate of formation in some cases is quite slow.

The object of this invention is to obviate these disadvantages by employing an electrolytic cell wherein both copper and graphite anodes separated from the iron cathodes by means of diaphragms are connected to two separate electrical circuits and neutral or alkaline brine is fed to the cathode chambers and drawn out from the anode chamber alongwith the product formed.

To these ends, the invention broadly consists in an electrolytic process wherein the cell employed is provided with both copper and graphite anodes separated from the iron cathodes by means of diaphragms. The copper and graphite anodes are connected in two separate electrical circuits. The current density at copper as well as

graphite anode is suitably adjusted at values of 5-10 amp/dm². Neutral or slightly alkaline brine (250 to 300 g/l) is fed to the cathode compartment and allowed to flow into the anode compartment through the diaphragms from where it is continuously drawn out alongwith the product formed. The cell is operated at temperatures between 30 and 70° C. The brine feed rate is maintained at desired values between 0.2 and 0.6 litre/ampere hour. The anolyte pH is maintained between 7 and 10. The cell effluent is fortified with sodium chloride after filtering off the copper oxychloride and fed back to the cell.

The following typical examples are given to illustrate the invention :

Example I

Electrolytic cell	A cylindrical PVC container of 5 litre capacity
Electrolyte	Brine : sodium chloride —250 g/l
Total current passed	8 amp
Anodes	Copper and graphite
Current density at copper	10 amp/dm ²
Current density at graphite	10 amp/dm ²
Cathodes	Iron
Diaphragm material	Asbestos cloth
Brine feed rate	0.4 l/amp-hr
Electrolyte temperature	32 ± 2°C.
Anolyte pH	7—10
Duration of electrolysis	6 hours
Weight of copper oxy-chloride formed	89 g.
Energy consumption	1.62 kwh/kg
Colour of the product formed	Emerald green
Percentage of Cu and Cl in the product	Cu: 59.4 Cl: 16.5

Example II

Electrolytic cell	A cylindrical PVC container of 5 liter capacity.
Electrolyte	Brine: Sodium chloride-300 g/l

Price : TWO RUPEES.

Total current passed	8 amp
Anodes	Copper and graphite
Current density at copper	6.66 amp/dm ²
Current density at graphite	10 amp/dm ²
Cathodes	Iron
Diaphragm material	Asbestos cloth
Brine feed rate	0.3 l/amp-hr
Electrolyte temperature	60±2°C
Anolyte pH	8-10
Duration of electrolysis	6 hours
Weight of copperoxychloride formed	101 g.
Energy consumption	1.22 kwh/kg
Colour of the product formed	Emerald green
Percentage of Cu and Cl in the product	Cu: 59.6 Cl: 16.6

The following are among the main advantages of the invention :

(1) The composition of copper oxychloride formed in this process is uniform throughout, the maximum variation not exceeding five percent. The colour of the product formed is uniformly emerald green.

(2) The formation of the product is accomplished in a single step.

Dated this 26th day of May, 1967.

(Sd./-)

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Council of Scientific and Industrial Research.

COMPLETE SPECIFICATION

AN ELECTROLYTIC PROCESS FOR THE PREPARATION OF COPPER OXYCHLORIDE

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI 1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860)

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :-

This is an invention by Sarvashri Srinivasa Sampath, Ramaswamy Thangappan Nadar, and Subramaniam Ramajayam, all of the Central Electrochemical Research Institute, Karaikudi-3, Madras State, India, all Indian Citizens.

This invention relates to an electrolytic process for the preparation of copper oxychloride which can be used as fungicide, pigment, wood preservative etc.

Hitherto, chemical methods have been proposed for making copper oxychloride by the interaction of copper with hydrochloric acid in the presence of air, or of a copper salt like cuprous chloride of copper sulphate with other suitable chemicals. In the electrochemical method the formation of copper oxychloride is reported by the electrolysis of sodium chloride solution at a very high current density at copper anode or at low current density and bubbling air. Copper oxychloride is also said to be formed by the electrolysis of a mixed electrolyte containing sodium chloride and sulphate at a copper anode in conjunction with an auxiliary graphite anode.

The processes known hitherto suffer from the drawbacks that the copper oxychloride formed varies widely in the contents of copper and chlorine (copper 52 to 68% and chloride 7 to 31%) depending on the reactants and conditions of reaction; the chemical method of preparation involves a number of steps and the rate of formation in some cases is quite low. The use of sulphate in the electrolyte results in the contamination of the product.

The object of this invention is to obviate these disadvantages by employing an electrolytic cell wherein both copper and graphite anodes separated from the iron cathodes by means of

diaphragms are connected to two separate electrical circuits and neutral or alkaline brine is fed to the cathode chambers and drawn out from the anode chamber along with the product formed.

The main finding underlying the invention consists in bringing together the copper anodically dissolved and the chlorine evolved into chemical reaction in the right proportion and under the right condition by means of the twin electrical circuit.

The use of two separate electrical circuits constitutes the novel aspect of the invention and this has resulted in a product of uniform quality in respect of composition and colour. This aspect has not been reported earlier.

Control of the alkalinity of the anolyte has also been found to be necessary in order to control the quality of the product.

The present invention consists of a continuous electrolytic process for the preparation of copper oxychloride wherein an electrolytic cell is employed with copper and graphite anodes and iron cathodes separated by porous diaphragms, the copper and graphite anodes being connected with independent sets of iron cathodes, in two separate electrical circuits, the current density at each of these two anodes being maintained at 5-10 amp/dm², the electrolyte (neutral or alkaline brine containing 250 to 300 g/l sodium chloride) being fed into the cathode compartments at a predetermined rate (0.2 to 0.6 l per amp. hr.) and allowed to flow through the diaphragms into the anode compartment wherefrom it is continuously withdrawn from the cell along with the product formed, the temperature of electrolysis being maintained at a value between 30 and 70° C.

the pH of the anolyte being 7-10 and the cell effluent after separation of the product being fortified with sodium chloride and fed back into the cell, and wherein the above electrolytic cell is used in conjunction with auxiliary equipment to carryout filtration, drying and grinding of the product.

The rate of flow of the electrolyte uniformly into the cathode compartments is maintained at a predetermined level by the use of a constant head tank. This is important in order to have a strict control over the quality of the product.

Detailed description of the process: The flow-sheet of the process is given in the attached drawing (Sheet No.1). The electrolytic cell (1) consists of a vessel of rectangular shape at bottom to facilitate withdrawal of the cell liquor along with the product formed, the cell being made of suitable material like reinforced cement concrete or PVC. Two sets of anodes, one of copper (2) and the other of graphite (4) are placed in the cell. The two sets of iron cathodes (3) are enclosed in diaphragms of suitable material such as asbestos or cotton fabric or PVC (5). The copper anodes are electrically connected with the contiguous iron cathodes in one circuit. A second electrical circuit connects up the graphite anodes and the other set of iron cathodes. Facilities are provided to control the direct current values in the two circuits independently. The electrolyte (salt solution) at the desired temperature is fed into the cathode compartments (within the diaphragms) at the predetermined rate. The electrolyte along with the product is withdrawn from the bottom of the cell and is fed into a filter (6) to separate the product and the electrolyte. The filtrate is collected in a storage tank (10) provided with heating coils. The contents are fortified with make-up salt, and heated. The solution flows into a sump tank (11) and is then pumped (12) to constant head tank (13) overhead. The level of the constant head tank is maintained by means of the overflow pipe.

The product after being washed free of adhering electrolyte in the filter is transferred to a dryer (7). The dry product is ground and sieved (8) prior to packing (9).

The following typical examples are given to illustrate the invention:

Example I

Electrolytic cell	A cylindrical PVC container of 5 litre capacity
Electrolyte	Brine : Sodium Chloride-250 g/l
Total current passed	8 amp.
Anodes	Copper and graphite
Current density at copper	10 amp/dm ²
Current density at graphite	10 amp/dm ²
Cathodes	Iron
Diaphragm material	Asbestos cloth
Brine feed rate	0.4 l/amp. hr.
Electrolyte temperature	32 ± 2 °C
Anolyte pH	7-10
Duration of electrolysis	6 hours
Weight of copper oxychloride formed	89 g.
Energy consumption	1.67 kwh/kg
Colour of the product formed	Emerald Green
Percentage of Cu and Cl in the product	Cu : 59.4 Cl : 16.5

Example II

Electrolytic cell	A cylindrical PVC container of 5 litre capacity
Electrolyte	Brine : Sodium chloride-300 g/l
Total current passed	8 amp
Anodes	Copper and graphite
Current density at copper	6.66 amp/dm ²
Current density at graphite	10 amp/dm ²
Cathodes	Iron
Diaphragm material	Asbestos cloth
Brine feed rate	0.3 l/amp-hr.
Electrolyte temperature	60 ± 2 °C
Anolyte pH	8-10
Duration of electrolysis	6 hours
Weight of copper oxychloride formed	101 g.
Energy consumption	1.22 kwh/kg
Colour of the product formed	Emerald green
Percentage of Cu and Cl in the product	Cu : 59.6 Cl : 16.6

The main advantages of this invention are :

(i) The composition of copper oxychloride formed in this process is uniform throughout, the maximum variation not exceeding 5%. The colour of the product formed is uniformly emerald green.

(ii) The product conforms to Indian Standard Specification.

(iii) The formation of the product is accomplished in a single step.

The process developed and invented is found to be more convenient to operate and control than the processes reported hitherto. The uniformity of the product, as obtained using this process, is essential when the product is included in fungicidal formulations.

WE CLAIM :

1. A continuous electrolytic process for the preparation of copper oxychloride wherein an electrolytic cell is employed with copper and graphite anodes and iron cathodes separated by porous diaphragms, the copper and graphite anodes being connected with independent sets of iron cathodes in two separate electrical circuits, the current density at each of these two anodes being maintained at 5-10 amp/dm², the electrolyte (neutral or alkaline brine containing 250-300 g/l sodium chloride) being fed into the cathode compartments at a predetermined rate (0.2 to 0.6 l per amp. hr.) and allowed to flow through the diaphragms into the anode compartment wherefrom it is continuously withdrawn from the cell along with the product formed, the temperature of electrolysis being maintained at a value between 30 and 70° C, the pH of the anolyte being 7-10 and the cell effluent after separation of the product being fortified with sodium chloride and fed back into the cell, and wherein the above electrolytic cell is used in conjunction with auxiliary processing equipment to carry out filtration, drying and grinding of the product.

2. A process as claimed in Claim 1 where copper and graphite anodes are used in the electrolytic cell.

3. A process as claimed in Claim 1 where iron cathodes enclosed in porous diaphragms

(of asbestos or cotton fabric or PVC) are used in the electrolytic cell.

4. A process as claimed in any of the preceding claims where copper and graphite anodes are electrically connected with different iron cathodes in separate circuits for passing the direct current for electrolysis.

5. A process as claimed in any of the preceding claims wherein the current densities at the copper and graphite anodes are maintained at 5 to 10 amp/dm².

6. A process as claimed in any of the preceding claims wherein the electrolyte used is neutral or alkaline brine containing 250-300 g/l sodium chloride.

7. A process as claimed in any of the preceding claims wherein the electrolyte is fed into the cathode compartments at a predetermined rate of 0.2—0.6 l/amp. hr. and allowed to flow through the diaphragm into the anode compartment.

8. A process as claimed in any of the previous claims where the temperature of electrolysis is maintained at a value between 30 and 80°C.

9. A process as claimed in any of the previous claims wherein the pH of the anolyte is maintained between 7 and 10.

10. A process as claimed in any of the preceding claims where the product is continuously withdrawn, as and when formed, along with the anolyte.

11. A process as claimed in any of the preceding claims wherein the electrolyte after separation of the product is fortified with sodium chloride and recycled into the cell.

12. A process as claimed in any of the preceding claims wherein the filtered product is washed, dried and ground to size.

13. A process as claimed in any of the preceding claims wherein is employed an electrolytic cell wherein both copper and graphite anodes separated from the iron cathodes by means of diaphragms are connected to two separate electrical circuits and neutral or alkaline brine is fed to the cathode chambers and drawn out from the anode chamber along with the product formed.

14. A process as claimed in claim 13 wherein the copper anodically dissolved and the chlorine evolved are brought together into chemical reaction by means of the twin electrical circuit.

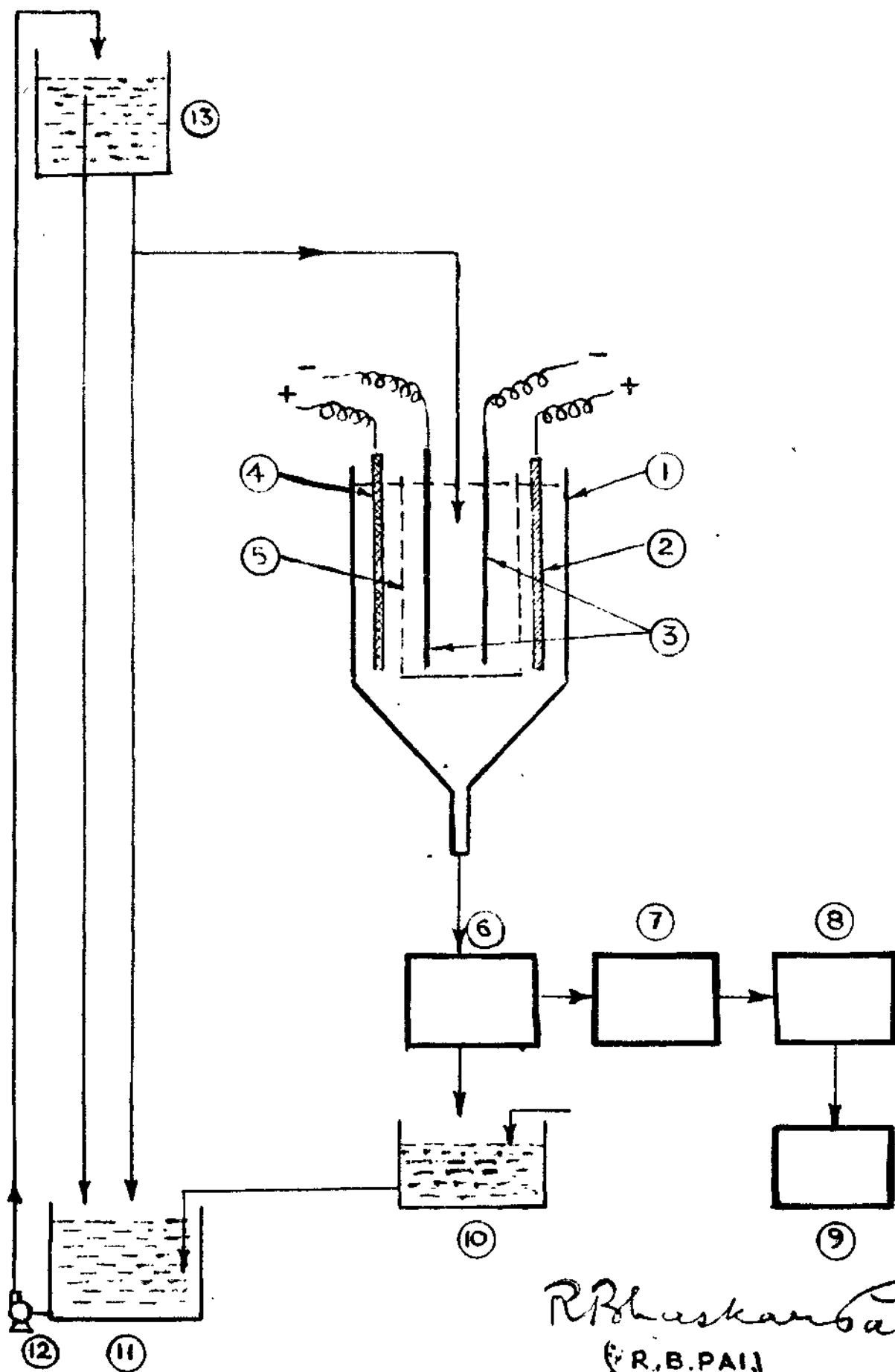
15. A process for the preparation of copper oxychloride substantially as hereinbefore described.

Dated this 23rd day of February, 1968.

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