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70B [LVIII (5)]

"IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC REDUCTION OF TITANIC SULPHATE TO
TITANOUS SULPHATE."

Council of Scientific & Industrial Research, Rafi Marg, New Delhi, India, an Indian Registered body incorporated under
the Registration of Societies Act, Act XXI of 1860.

This is an invention by Handady Venkatakrishna Udupa, Director, Kapisthalam Chetlur Narasimham, Scientist, and
Srinivasaraghavan Vasundara, Senior Laboratory Assistant, all of Central Electrochemical
Research Institute, Karaikudi—3, Tamil Nadu, all Indians.

PROVISIONAL

The following specification describes the nature of this invention :

This invention relates to the improvements in or relating to the electrolytic reduction of titanic sulphate to titanous sulphate.

Hitherto it has been the practice to prepare titanous sulphate by reducing dilute titanic sulphate chemically with lead or zinc amalgams and no detailed literature is available for the reduction of titanic sulphate solution electrolytically except that amalgamated lead cathode can be used in a divided cell. (Ref. G. Brauer, Handbook of preparative inorganic chemistry, Vol. II, Academic Press, New York, 1965, p. 1226).

The objections to the current practice are as follows :

As there are no data and conditions available for electrolytic reduction of titanic sulphate, it is not possible to give any objections to the current practice. However, according to the method worked out by B. Diethelm and F. Foerster, only dilute solution having a concentration of 18 g. of TiO_2 /litre was used for the reduction.

The object of this invention is to obviate these disadvantages by working out the following modified procedure.

The electrolytic reduction of titanic sulphate is carried

out in a cell using a lead anode and lead, copper, zinc or graphite as cathodes with and/or without amalgamation at a temperature ranging from 25° to 60°C . A cathode current density of 0.5 to 10 amp/dm² is used. The current efficiency and yield are higher with rotating cathode than with a stationary cathode.

The titanic sulphate solution containing 120 to 480 g/l $\text{Ti}(\text{SO}_4)_2$ (i.e. 40 to 160 g/l equivalent of TiO_2) and 160 to 800 g/l sulphuric acid, was electrolysed in an electrolytic cell consisting of lead anode and lead, copper zinc or graphite cathodes. A porous pot, blue asbestos cloth, terylene, microporous rubber or blue asbestos thread wound on the anode acted as diaphragms and prevented the reoxidation of the catholyte of titanous sulphate solution. An inert atmosphere, such as of carbon dioxide was maintained during electrolysis to prevent oxidation of titanous sulphate by air. The cathode was kept either in stationary or in rotating motion. The current efficiency and yield were calculated on the basis of titanous sulphate formed. Complete conversion of titanic sulphate is possible by passing excess quantity of electricity of the order of 20 to 35% in the case of rotating cathode.

Examples : Vide separate sheets attached (Tables 1 & 2).

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TABLE 1

	Example I	Example II	Example III	Example IV	Example V	Example VI	Example VII
1. Concentration of catholyte—TiO ₂ g/l.	73.4	68.2	101.8	64.3	64.3	52.1	68.2
Equivalent of Ti(SO ₄) ₂ —g/l	220.2	204.5	305.4	192.7	192.7	156.4	204.5
Sulphuric acid—g/l	328	328	446.8	328	328	218.7	328
2. Anolyte.	20% H ₂ SO ₄	20% H ₂ SO ₄	No separate anode chamber	No separate anode chamber	No Separate anode chamber	20% H ₂ SO ₄	20% H ₂ SO ₄
3. Anode	Lead	Lead	Lead	Lead	Lead	Lead	Lead
4. Cathode	Amalgamated lead Rotation	Amalgamated lead Stationary	Amalgamated lead Rotation	Amalgamated copper Rotation	Graphite Rotation	Amalgamated lead Rotation	Amalgamated lead Rotation
5. Diaphragm	Porous pot	Porous pot	Blue asbestos thread wound over lead anode	Blue asbestos thread wound over lead anode	Blue asbestos thread wound over lead anode	Porous pot	Microporous rubber
6. Cathode current density—amp/dm ²	10	5	5	5	5	1	5
7. Bath voltage (V)	3.3	3.0	3.32	3.2	4.1	2.6	4.3
8. Temperature (°C)	30—40	60	60	30—35	30—32	35	30—32
9. Percentage yield of titanous sulphate.	86.8	82.17	87.7	78.77	82.5	79.49	91.33
10. Energy consumption D.C. (Kwh/kg of Ti ₂ (SO ₄) ₃).	0.34	0.26	0.27	0.28	0.35	0.23	0.33

TABLE 2

	Example		Example		Example		Example	
	IA	IB	IIA	IIB	IIIA	IIIB	IVA	IVB
1. Concentration of catholyte—TiO ₂ g/l	91.04	91.04	101.8	101.8	68.16	68.16	76.2	76.2
Equivalent of Ti(SO ₄) ₂ —g/l.	273.12	273.12	305.4	305.4	204.48	204.5	228.6	228.6
Sulphuric acid—g/l.	437.3	437.3	446.8	446.8	328.0	328.0	335.1	335.1
2. Anode	Lead	Lead	Lead	Lead	Lead	Lead	Lead	Lead
3. Cathode	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead
4 Motion of cathode	Stationary	Rotation	Stationary	Rotation	Stationary	Rotation	Stationary	Rotation
5. Diaphragm	Porous pot.	Porous pot	Blue asbestos wound over the anode	Blue asbestos wound over the anode	Porous pot	Porous pot	Blue asbestos wound over the anode	Blue asbestos wound over the anode
6. Temperature (°C)	30—35	30—35	60	60	60	60	60	60
7. Current efficiency (%)	59.94	78.38	66.89	87.82	79.38	89.89	74.09	89.41
8. Percentage yield of titanous sulphate	60.06	78.56	66.79	87.70	82.10	93.05	74.11	89.43

The following are the main advantages of the invention :

(1) Titanic sulphate solution of 120 to 480 g/l (i.e. corresponding to 40 to 160 g/l TiO_2) and containing 160 to 800 g/l sulphuric acid can be reduced electrolytically to titanous sulphate.

(2) The electrolytic reduction takes place with a higher current efficiency and yield at a rotating amalgamated lead cathode.

(3) A wide range of cathode current density of 0.5 to

10 amp/dm² can be employed and the rotation of the cathode enables the use of higher current density than the conventional one.

(4) A wide range of temperature of 25° to 60°C can be employed.

(5) Blue asbestos thread wound on the anode can be used to prevent the oxidation of titanous sulphate solution formed and this will simplify the scaling-up problem as regards the choice of diaphragm.

Dated this 5th day of March, 1970.

COMPLETE

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

(1) This invention relates to the improvements in or relating to the electrolytic reduction of titanous sulphate to titanous sulphate suitable as a reducing agent.

(2) Hitherto it has been the practice to prepare titanous sulphate by reducing dilute titanous sulphate chemically with lead or zinc amalgams or electrolytically and no detailed literature is available for the reduction of titanous sulphate solution electrolytically except that amalgamated lead cathode can be used in a divided cell.

(3) The objections to the current practice are as follows : As there are no data and conditions available for electrolytic reduction of titanous sulphate, it is not possible to give any objections to the current practice.

(4) The object of the invention is to establish the operating conditions for the reduction of fairly concentrated solution of titanous sulphate which gives maximum yield with improving current efficiency by rotating the cathode and simplifying the cell set-up.

According to the present invention there is provided a process for the electrolytic reduction of titanous sulphate to titanous sulphate which comprises in electrolysis a titanous sulphate solution containing 120 to 480 g/l $\text{Ti}(\text{SO}_4)_2$ and 160 to 800 g/l sulphuric acid in a divided cell using lead anode and lead or amalgamated lead cathode wherein the cathode is rotated and blue asbestos thread is wound over the lead anode to act as diaphragm, a cathode current density of 0.5 to 10 amp/dm² and a temperature of 25° to 60°C are employed, the reduction is carried out in an inert atmosphere.

(5) The electrolytic reduction of titanous sulphate is carried out in a cell using a lead anode and lead, copper, zinc or graphite as cathode with/ or without amalgamation at a temperature ranging from 25° to 60°C. A cathode current density of 0.5 to 10 amp/dm² is used. The current

efficiencies are higher with rotating cathode than with a stationary cathode.

The titanous sulphate solution containing 120 to 480 g/l $\text{Ti}(\text{SO}_4)_2$ (i.e. 40 to 160 g/l equivalent of TiO_2) and 160 to 800 g/l sulphuric acid, was electrolysed in an electrolytic cell consisting of lead anode and lead, copper, zinc or graphite cathodes. A porous pot, blue asbestos cloth, terylene, microporous rubber or blue asbestos thread wound over the anode acted as diaphragms and prevented the reoxidation of the catholyte of titanous sulphate solution. An inert atmosphere, such as carbon dioxide was maintained during electrolysis to prevent oxidation of titanous sulphate by air. The cathode was kept either stationary or rotating. The current efficiency and yield were calculated on the basis of titanous sulphate formed. Complete conversion of titanous sulphate is possible by passing excess quantity of electricity of the order of 20 to 35% in the case of rotating cathode.

(6) The electrolytic reduction of titanous sulphate containing 120 to 480 g/l $\text{Ti}(\text{SO}_4)_2$ (i.e. 40 to 160 g/l equivalent of TiO_2) and 160 to 800 g/l sulphuric acid in an electrolytic cell consisting blue asbestos thread wound over the lead anode and employing a rotating amalgamated lead cathode form the novel features of the invention.

When rotating cathode is employed the current efficiency and yield are always higher at least by 10 to 15% than with a stationary cathode (vide following Table II). The rotating cathode makes it possible to employ higher cathode current density viz. 3 to 10 amp/dm² without sacrificing the yield to a large extent. However, with stationary cathode, a current density of 1 to 5 amp/dm² can be employed (Vide following Table I).

(7) The use of blue asbestos thread wound over the lead anode as diaphragm simplifies the scale-up of the process.

TABLE 1

	Example I	Example II	Example III	Example IV	Example V	Example VI	Example VII
1. Concentration of catholyte— TiO_2 (g/l.)	73.4	68.2	101.8	64.3	64.3	52.1	68.2
Equivalent of $\text{Ti}(\text{SO}_4)_2$ (g/l.)	220.2	204.5	305.4	192.7	192.7	156.4	204.5
Sulphuric acid (g/l.)	328	328	446.8	328	328	218.7	328
2. Anolyte.	20% H_2SO_4	20% H_2SO_4	No separate anode chamber	No separate anode chamber	No separate anode chamber	20% H_2SO_4	20% H_2SO_4
3. Anode	Lead	Lead	Lead	Lead	Lead	Lead	Lead
4. Cathode	Amalgamated lead Rotation	Amalgamated lead Stationary	Amalgamated lead Rotation	Amalgamated copper Rotation	Graphite Rotation	Amalgamated lead Rotation	Amalgamated lead Rotation
5. Diaphragm	Porous pot	Porous pot	Blue asbestos thread wound over lead anode	Blue asbestos thread wound over lead anode	Blue asbestos thread wound over lead anode	Porous pot	Microporous rubber
6. Cathode current density (amp/dm ²)	10	5	5	5	5	1	5
7. Bath voltage (V)	3.3	3.0	3.32	3.2	4.1	2.6	4.3
8. Temperature (°C)	30–40	60	60	30–35	30–32	35	30–32
9. Percentage yield of titanous sulphate.	86.8	82.17	87.7	78.77	82.5	79.49	91.33
10. Energy consumption DC (Kwh/kg of $\text{Ti}_2(\text{SO}_4)_3$).	0.34	0.26	0.27	0.28	0.35	0.23	0.33

TABLE 2

	Example			Example			Example			** Example		
	IA	IB	IIC	IIA	IIB	IIIC	IVA	IVB	IVC	VA	VB	VC
1. Concentration of catholyte— TiO_2 (g/l.)	91.04	91.04	101.8	101.8	101.8	101.8	68.16	68.16	68.16	101.6	96.4	96.4
Equivalent of $\text{Ti}(\text{SO}_4)_2$ (g/l.)	273.12	273.12	305.4	305.4	305.4	305.4	204.48	204.48	204.48	304.8	289.2	289.2
Sulphuric acid (g/l.)	437.3	437.3	446.8	446.8	446.8	446.8	328.0	328.0	328.0	434.0	434.0	434.0
2. Anode	Lead	Lead	Lead	Lead	Lead	Lead	Lead	Lead	Lead	Lead	Lead	Lead
3. Cathode	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead	Amalgamated lead
4. Motion of cathode	Stationary	Rotation	Stationary	Stationary	Rotation	Rotation	Stationary	Stationary	Stationary	Stationary	Stationary	Rotation
5. Diaphragm	Porous pot	Porous pot	Blue asbestos wound over the anode	Blue asbestos wound over the anode	Blue asbestos wound over the anode	Blue asbestos wound over the anode	Blue asbestos wound over the anode	Blue asbestos wound over the anode	Blue asbestos wound over the anode	Blue asbestos wound over the anode	Blue asbestos wound over the anode	Blue asbestos wound over the anode
6. Temperature (°C)	30–35	30–35	60	60	60	60	60	60	60	60	60	60
7. Current efficiency (%)	59.94	78.38	66.89	87.82	79.38	89.89	74.09	89.41	89.41	66.2	85.5	85.5
8. Percentage yield of titanous sulphate	60.06	78.54	66.79	87.7	82.1	93.05	74.11	89.43	89.43	65.9	85.1	85.1

** Results of large scale experiments.

(8) The present invention consists of a process for the electrolytic reduction of titanic sulphate to titanous sulphate which comprises in electrolysing a titanic sulphate solution containing 120 to 480 g/l $\text{Ti}(\text{SO}_4)_2$ and 160 to 800 g/l sulphuric acid in a divided cell using lead anode and lead or amalgamated lead cathode wherein the cathode is rotated and blue asbestos thread is wound over the lead anode to act as diaphragm. A cathode current density of 0.5 to 10 amp/dm² and a temperature of 25° to 60°C are employed. The reduction is carried out in an inert atmosphere.

(9) It is possible to prepare higher concentrations of titanic sulphate solution which can be used as a reducing agent. Complete conversion of titanic sulphate is possible by passing excess quantity of electricity of the order of 20 to 35% in the case of rotating cathode.

(10) The flow diagram is given in the attached figure.

(11) A few typical examples to illustrate the process are given in Tables I and II. Table II, example V gives the typical results of large scale experiments viz., 100 ampere cell, with 25 litres of titanic sulphate solution containing 90–110 g/l TiO_2 and 350 to 450 g/l sulphuric acid.

(12) The following are the main advantages of the invention :

(i) High concentrations of titanic sulphate solution of 120 to 480 g/l (i.e. corresponding to 40 to 160 g/l TiO_2) containing 160 to 800 g/l sulphuric acid can be reduced electrolytically to titanous sulphate at a temperature range of 25° to 60°C.

(ii) The electrolytic reduction takes place with a higher current efficiency and yield at a rotating amalgamated lead cathode (Refer Table II).

(iii) A wide range of cathode current density of 0.5 to 10 amp/dm² can be employed and the rotation of the cathode enables the use of higher current density than the conventional one.

(iv) Blue asbestos thread wound on the anode can be used to prevent the oxidation of titanous sulphate solution formed and this will simplify the scaling-up problem as regards the choice of diaphragm.

(13) The present invention relates to the electrolytic reduction of titanic sulphate solution of 120 to 480 g/l (corresponding to 40 to 160 g/l TiO_2) containing 160 to 800 g/l sulphuric acid in a cell having blue asbestos thread wound lead anode and a rotating amalgamated lead cathode at a current density of 0.5 to 10 amp/dm² and a temperature of 25° to 60°C. The reduction is carried out in an inert

atmosphere. Complete conversion of titanic sulphate is possible by passing excess quantity of electricity of the order of 20 to 35% in the case of rotating cathode.

WE CLAIM

(1) A process for the electrolytic reduction of titanic sulphate to titanous sulphate which comprises in electrolysing a titanic sulphate solution containing 120 to 480 g/l $\text{Ti}(\text{SO}_4)_2$ and 160 to 800 g/l sulphuric acid in a divided cell using lead anode and lead or amalgamated lead cathode wherein the cathode is rotated and blue asbestos thread is wound over the lead anode to act as diaphragm, a cathode current density of 0.5 to 10 amp/dm² and a temperature of 25° to 60°C are employed, the reduction is carried out in an inert atmosphere.

(2) A process as claimed in claim (1) wherein the titanic sulphate solution of 120 to 480 g/l (corresponding to 40 to 160 g/l TiO_2) containing 160 to 800 g/l sulphuric acid is reduced electrolytically.

(3) A process as claimed in claim (1) wherein lead, copper, zinc or graphite is used as cathode, the first three electrodes are used either with or without amalgamation.

(4) A process as claimed in claim (1) and (3) wherein the cathode is rotated or kept stationary.

(5) A process as claimed in claim (1) wherein a porous pot, blue asbestos cloth, terylene, microporous rubber or blue asbestos thread wound over the anode acts as a diaphragm to prevent the reoxidation of the reduced titanous sulphate.

(6) A process as claimed in claim (1) wherein the electrolytic reduction is carried out at a wide cathode current density range of 0.5 to 10 amp/dm² and the rotation of the cathode enables the use of higher current density than the conventional one.

(7) A process as claimed in claim (1) wherein titanic sulphate is completely reduced.

(8) A process for the electrolytic reduction of titanic sulphate to titanous sulphate as substantially hereinbefore described.

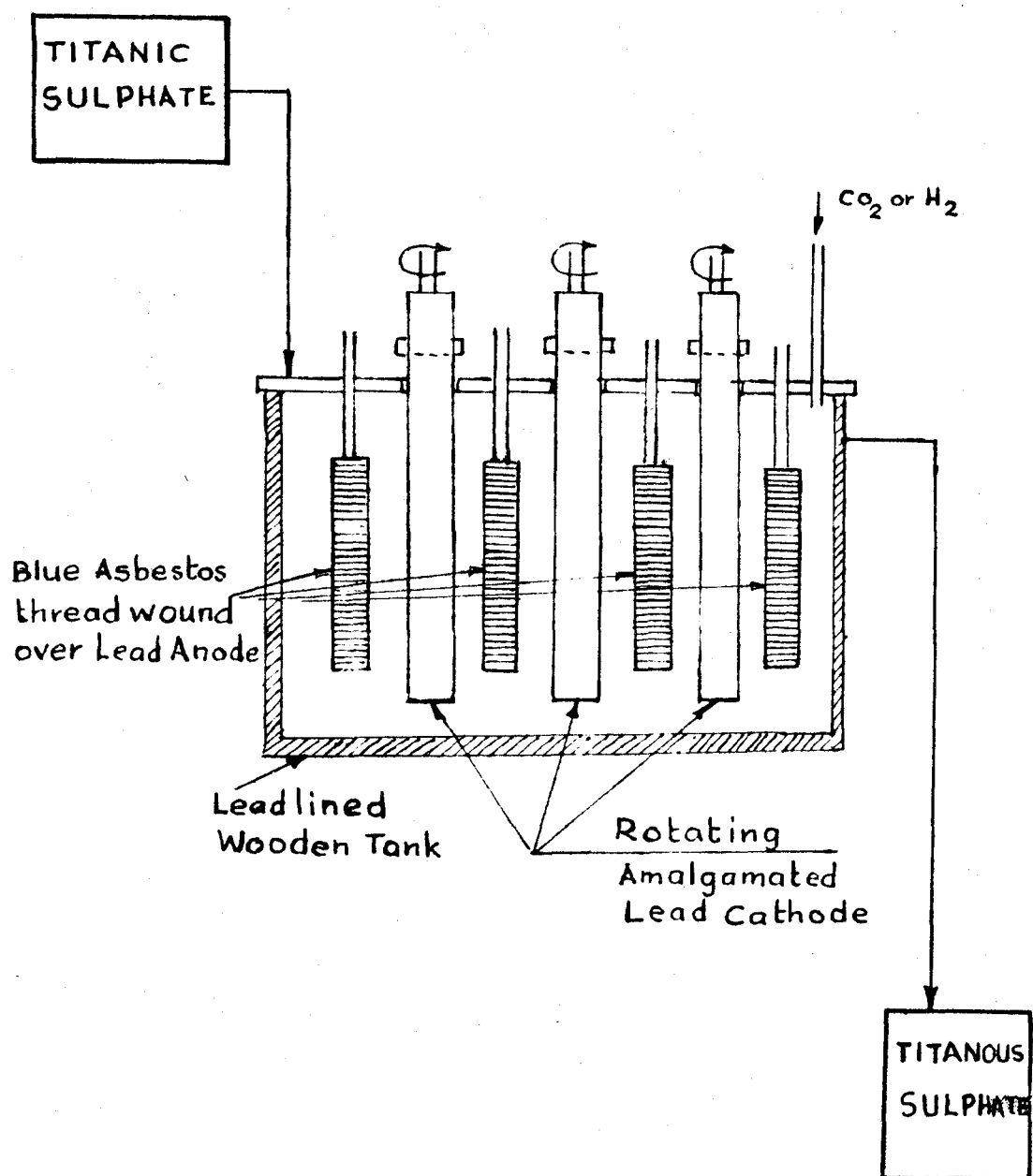
Dated this 21st day of December, 1970.

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