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ELECTROCHEMICAL SYNTHESIS OF ERYTHROSINE

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Studies were made with rotating graphite, graphite substrate lead dioxide (GSLD) and RuO_2/Ti anodes at different conditions to arrive at maximum yield of erythrosine. Photomicrographs of the RuO_2 coated titanium anode before and after use are included. IR measurements of the finished product are compared with the commercially available sample. Maximum yield and dye content have been obtained with RuO_2/Ti anode.

Key words: Erythrosine, rotating anode, electro-oxidation, graphite substrate lead dioxide anode, RuO_2 - Ti anode

INTRODUCTION

It was observed [1] earlier that the use of rotating anode gave better yield than at stationary anode for the preparation of erythrosine. With a view to optimise the conditions for getting maximum yield of erythrosine with a dye content not less than 85%, experiments were done by varying the parameters like electrolyte composition, current density, quantity of electricity at anodes like graphite, graphite substrate lead dioxide (GSLD) and RuO_2 coated titanium (titanium metal - anode) using rotation for the anode. It is reported that the sodium or potassium salt of tetra iodofluorescein gives 2 absorption bands in dilute solutions, the one extending from λ488 to λ530, then the narrower band between λ 550 to λ 558 [2]. The erythrosine was analysed by the same procedure described in ISI [3]. The same property of aniline converting to p-iodoaniline on reaction with iodine in the presence of aqueous sodium bicarbonate [4] has been made use of for the preparation of erythrosine by electrolytic method.

EXPERIMENTAL

Three electrodes viz. graphite, GSLD, [5] and ruthenium oxide coated titanium were used with rotation and iodination was done. The cell was a 1- litre beaker with a ceramic diaphragm to separate catholyte from anolyte and in which a stainless steel strip acted as cathode. Iodination was done electrochemically in the cell using an anolyte of 500 ml solution containing sodium bicarbonate, iodine and fluorescein. The catholyte was 100 ml of sodium bicarbonate solution. The strength of the solution was varied in each experiment. After passing the theoretical quantity of electricity (8F/mole fluorescein) the solution was filtered, and neutralised with acid to liberate the dye viz. tetra iodofluorescein which was then filtered, dried and weighed. The sample was tested for dye content by spectrophotometry. The solution left after removal of dye was estimated for iodate by iodimetry.

TABLE-I: Iodination of fluorescein at a rotating graphite anode
Anolyte: 500 ml water containing 50 g sodium bicarbonate;
Catholyte: 100 ml water containing 10 g sodium bicarbonate;
Current: 5A; C.D.: 0.7 kA.m^{-2}; Temperature: 313 - 323K; Voltage: 9 -12V

No.	Wt. of fluorescein (g)	Wt. of iodine (g)	Wt. of KI (g)	Wt. of iodate (g)	Wt. of erythrosine (g)	Dye content (%)	Insolubles (g)	Yield (%)	Current efficiency (%)
1	40	27	-	2.77	32.0	86.0	10.6	32	29.2
2	30	20	-	0.12	31.0	65.7	3.3	46.5	57.8
3	20	13.5	-	1.47	16.6	84.3	2.4	37.3	34.0
4	40	6.0*	106	-	53.8	53.7	4.0	60.5	55.0
5	90	3.7*	70.6	0.9	4.6	69.4	2.7	46.8	42.7

* Free iodine (Voltage 5 - 10 V)

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RESULTS AND DISCUSSION

Experiments with graphite anode

The experimental conditions and results are given in Table I for rotating graphite anode.

From the data, it is evident that the results are inconsistent due to disintegration of graphite anode. Since the dye content is not upto the mark with potassium iodide further studies were discontinued. When experiment was carried out with stationary graphite anode using 1500 ml of water containing 150 g of $NaHCO_3$ + 100 g fluorescein + 67.5 iodine as anolyte and 200 ml of water containing 20 g $NaHCO_3$ as catholyte and employing a current density of 0.5kA.m^{-2} (current 10 A), at temperature of 313-323K, a low yield of erythrosine (30.3% and weight 67.3g) with a current efficiency of 27.4% and having a dye content of 52% could alone be obtained.

Experiments with GSLD anode

The conditions and results of the experiments employing GSLD anode are shown in Table II.

TABLE-II: Iodination of fluorescein at a rotating GSLD anode (Conditions same as in Table I) Voltage: 5 - 10V

No.	Wt. of fluorescein (g)	Wt. of iodine (g)	Insolubles (g)	Wt. of iodate (g)	Wt. of erythrosine (g)	Dye content (%)	Yield (%)	Current efficiency (%)
1	40	27.0	2.9	10.0	33.5	74	40.6	39.0
2	30	20.0	1.7	4.3	27.7	85	51.0	41.5
3	20	13.5	0.98	3.7	14.2	100	50.0	32.0

Although the dye content is quite satisfactory at a GSLD anode, the sample of erythrosine when examined for lead by atomic absorption spectrophotometer contained lead to the extent of 74 ppm. The permitted level by I.S.I. specification is 10 ppm. The erythrosine sample obtained by the above method was dissolved in alkali and after filtration and reprecipitation the lead content was found to be 23 ppm.

Experiments with RuO_2 coated titanium anode

The growing interest in ruthenium oxide coated titanium anode is due to their ability to work well as anode at high current densities in chlor alkali cells [6]. Since graphite is not able to withstand the conditions and GSLD anode was not suitable due to lead contamination, RuO_2 coated titanium was used for the studies. As regards the toxicity of ruthenium it is reported [7] as probably toxic but such small amounts are used industrially that it does not constitute a hazard.

Iodination of fluorescein was done at a RuO_2 coated titanium anode using rotation and the results are presented in Table III.

When estimated for iodide [8] after removal of erythrosine the solution contained no iodide showing that all iodine must have been converted to as iodate or in the dye or present in the free form to some extent.

CONCLUSION

Graphite anode gives erythrosine of required dye content (85%) under rotation but the anode gets disintegrated due to simultaneous oxygen evolution. GSLD anode also gives erythrosine under similar conditions but the dye is contaminated with lead and even after recrystallisation it does not satisfy the I.S.I. specification. Use of potassium iodide is not giving the erythrosine of the required dye content. Ruthenium oxide coated titanium anode gives erythrosine of required dye content. The surface changes due to use of the RuO_2 coated titanium anode in electrolysis were examined using scanning electron microscope (SEM) (Fig.1) show that there is no change before and after use. The finished product, erythrosine, was compared with the commercial sample by infrared spectroscopy (Fig.2) and the results show that there is no change in the peak characteristics.

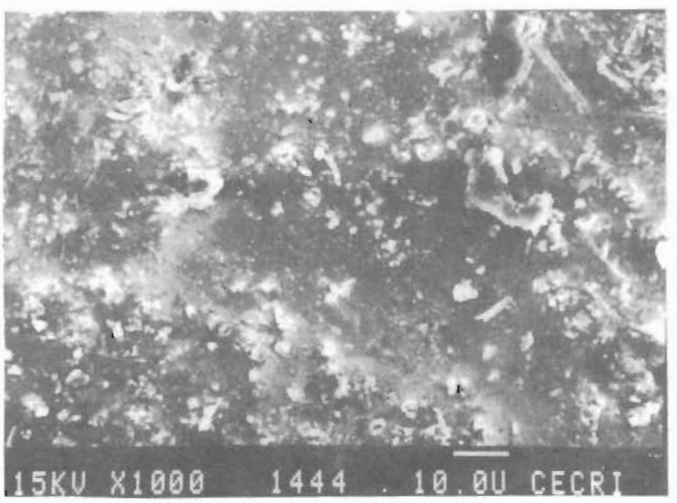

Fig.1: SEM photograph of RuO_2 deposited titanium anodes before (1444) use in iodination of fluorescein: 1000 times magnification.

TABLE-III: Iodination of fluorescein at a rotating RuO_2 coated titanium anode
Anolyte: 500 ml water containing 50 g sodium bicarbonate + 40 g fluorescein + 27 g iodine; Catholyte: 100 ml water containing 10 g sodium bicarbonate; Current: 4A; C.D. 0.6 kA.m^{-2}; Temperature: 313 -323 K ; Voltage 7- 12 V

No.	Fraction of theoretical qty. of current (1 = 8F)	Insolubles (g)	Wt. of free I_2 (g)	Wt. of iodate (g)	Wt. of erythrosine (g)	Dye content (%)	Yield (%)	Current efficiency (%)
1	0.64	0.8	3.2	0.9	38.0	78.7	42.8	60.0
2	0.80	0.9	Nil	3.2	37.2	73.2	41.8	47.7
3	1.00	1.5	Nil	4.0	32.6	92.9	36.7	33.0

SEM photograph of RuO_2 deposited titanium anodes after use (1445) in iodination of fluorescein: 1000 times magnification

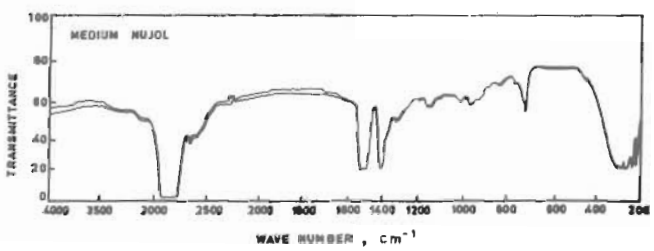

Fig.2: IR spectrum of erythrosine prepared and commercial one

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