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ENVIRONMENTALLY SAFE TECHNOLOGY
FOR SYNTHESIZING TITANIUM TRICHLORIDE
FOR THE NEEDS OF VARIOUS INDUSTRIES*E.N. Kuzin, T.I. Nosova, N.E. Kruchinina*

The authors have assessed the possibility of electrochemical synthesis of a wide range of reagents based on titanium trichloride as part of the work. Despite the growing demand for titanium trichloride and its derivatives, the production technology of this reagent has not been improved for a long period. Traditional technologies feature high environmental and industrial hazards, and the process itself has high energy consumption and a complex hardware scheme. As part of preliminary work, the possibility of obtaining titanium trichloride from aqueous solutions of titanium tetrachloride is established, while the proposed technology is distinguished by reduced energy consumption and safety. At the first stage of experiments in the anodic dissolution of aluminum, binary solutions of titanium trichloride and aluminum chloride are obtained. The degree of conversion $TiCl_4 \rightarrow -TiCl_3$ is 65%–35% for a current density of 10–30 A/dm², respectively. In the process of reducing an aqueous solution of titanium tetrachloride with iron electrodes, the yield of titanium trichloride is approximately 76%–66% for a current density of 10–30 A/dm², respectively. The resulting solution is heavily contaminated with iron (II) compounds. The results of the experiments show the high efficiency of this solution in the processes of purification of wastewater from galvanic production from chromium (VI) compounds. For the production of high-purity titanium trichloride, titanium electrodes are used, while the yield of titanium trichloride is 59%–3% for a current density of 10–30 A/dm², respectively. Depending on the production technology and electrode material, solutions are obtained that can be used to produce high-purity

titanium dioxide for the production of dye-sensitized solar cells, reagents for water purification, and a Ziegler-Natta catalyst and a reagent for organic synthesis.

Keywords: *catalyst; recovery; titanium trichloride*

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ЭКОЛОГИЧЕСКИ БЕЗОПАСНАЯ ТЕХНОЛОГИЯ СИНТЕЗА ТРЕХХЛОРИСТОГО ТИТАНА ДЛЯ НУЖД РАЗЛИЧНЫХ ОТРАСЛЕЙ ПРОМЫШЛЕННОСТИ

Е.Н. Кузин, Т.И. Носова, Н.Е. Кручинина

В рамках работы авторы оценили возможность электрохимического синтеза широкого спектра реагентов на основе трихлорида титана. Несмотря на растущий спрос на трихлорид титана и его производные, технология производства этого реагента долгое время не совершенствовалась. Традиционные технологии отличаются высокой экологической и промышленной опасностью, а сам процесс отличается высоким энергопотреблением и сложной аппаратной схемой. В рамках предварительной работы установлена возможность получения трихлорида титана из водных растворов тетрахлорида титана, при этом предлагаемая технология отличается сниженным энергопотреблением и безопасностью. На первом этапе экспериментов по анодному растворению алюминия получены бинарные растворы трихлорида титана и хлорида алюминия. Степень преобразования $TiCl_4 \rightarrow -TiCl_3$ составляет 65%–35% при плотности тока 10–30 А/дм² соответственно. В процессе восстановления водного раствора тетрахлорида титана железными электродами выход трихлорида титана составляет приблизительно 76%–66% при плотности тока 10–30 А/дм² соответственно. Полученный раствор сильно загрязнен соединениями железа (II). Результаты экспериментов показывают высокую эффективность этого решения в процессах очистки сточных вод гальванического производства от соединений хрома (VI). Для производства трихлорида титана высокой чистоты используются титановые электроды, при этом выход трихлорида титана составляет 59%–3% при плотности тока 10–30 А/дм² соответственно. В зависимости от технологии производ-

ства и материала электрода, можно получить растворы, которые могут быть использованы для получения диоксида титана высокой чистоты для производства солнечных элементов, сенсibilизированных к красителям, реагентов для очистки воды, а также катализатора Циглера-Натта и реагента для органического синтеза.

Ключевые слова: катализатор; восстановление; трихлорид титана

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Introduction

Over the past decade, the global consumption of titanium compounds for different industries has constantly increased. Among the crucial areas of their application, one should note pharmacology, medicine, optical instrumentation, polymer and food industry, and synthesis and use of nanomaterials.

Producing high-quality polymers and synthetic rubbers is impossible without a stereospecific Ziegler-Natta catalyst. The titanium trichloride complex and the organoaluminium compounds that are part of it are universal initiators of the polymerization process of unsaturated hydrocarbons. The discovery of this catalyst makes it possible to synthesize polypropylene, polyethylene, cis-1,4-polybutadiene, cis-1,4-polyisoprene, and other stereoregular vinyl derivatives [7]. It is why manufacturing polymer products, lubricants, synthetic oils, fabrics, membranes, coatings, and paints are impossible without a Ziegler-Natta catalyst [11].

Along with the production of polymers, titanium trichloride forms the basis of the anode coating in the electrolytic process to produce large-capacity products such as sodium hydroxide and chlorine. Additionally, titanium chloride (III) – the feedstock in preparing nano dispersed titanium dioxide – is the most valuable raw material for some chemical industries.

One of the most promising applications of nano dispersed titanium dioxide is the production of coatings for Dye-sensitized solar cells (DSSC). One should note that the classical technology for producing titanium dioxide nanoparticles from titanium tetrachloride is not suitable for this purpose, which is why titanium trichloride is used as a precursor [9].

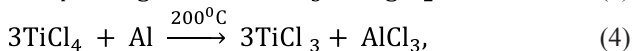
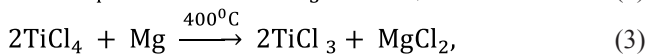
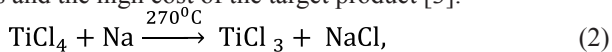
According to the results of separate studies, the possibility of using titanium trichloride as a wastewater treatment reagent has been confirmed. Research teams have proven the high efficiency of titanium trichloride-based coagulants

in the processes of removing chromium (VI) compounds from water [4] and dissolved organic compounds [8]. The addition of titanium compounds to classical coagulants based on aluminum and iron salts makes it possible to significantly intensify wastewater treatment processes of various origins [2; 10].

The chief industrial method for producing titanium (III) chloride abroad is based on the interaction with gaseous hydrogen according to reaction 1. This method, being practically the first one, has some significant drawbacks. The high price of hardware design and raw materials and the insecurity and complexity of the process are not the only disadvantages of this technology [3].



An alternative to expensive hydrogen can be various metals, namely sodium, magnesium, aluminum (reactions 2–4), etc. Nevertheless, the replacement of reducing agents cannot solve the primary issue associated with the harsh conditions of the process and the high cost of the target product [3].



There are studies in which the reducing agent is hydrochloric acid, wherein the process occurs at 70–80°C. The authors manage to reduce equipment costs by simplifying the production scheme significantly. However, the synthesis duration excludes the possibility of its implementation in industrial production [6].

Relatively recently, a technology for producing titanium trichloride based on the thermal reduction of an aqueous solution of titanium (IV) chloride using aluminum has been proposed [5]. The chief advantages of this technology include high environmental and industrial safety due to the refusal to use concentrated solutions of TiCl_4 and reduced energy consumption due to the synthesis in relatively mild conditions (up to 100°C without excessive pressure and inert atmosphere).

Notwithstanding, the preceding issue of finding new and promising low-cost technologies for titanium (III) chloride production remains extremely relevant.

Materials and methods

The primary research goal is to study the electrochemical variant of the synthesis of titanium trichloride by obtaining a wide range of products for various industries.

Experiments on the electrochemical reduction of titanium tetrachloride with various metals are carried out in an experimental reactor with a magnetic stirrer. The electrodes are placed at a distance of 5.5 cm and connected to a direct current source. With each of the selected metals, three series of experiments are performed with current densities of 10-30 A/dm². Samples are taken every ten minutes, and at the end of the synthesis, the defect of the mass of the electrodes is determined.

Aluminum (AD-31), iron (St3), and titanium (VT-1-0) plates are used as electrodes. The initial precursor for synthesizing titanium (III) chloride has been a low-concentration (2.5% by weight) aqueous solution of titanium tetrachloride. Such a concentration has been chosen as the most favorable for conducting experiments, since concentrated titanium (IV) chloride actively interacts with atmospheric moisture, forming toxic hydrochloric acid vapors, which causes the production hazard of the process. Aqueous solutions of titanium tetrachloride are prepared by slow dissolution of concentrated titanium tetrachloride in water acidulated with hydrochloric acid under continuous cooling [1].

The efficiency of the electrochemical reduction process is evaluated by reverse titration with a solution of potassium bichromate [3]. Determination of chromium (VI) is determined spectrophotometrically on the DR 2800 instrument (HACH USA). Total metal content in the solutions is determined on the "SpectroSky" atomic emission spectrometer (Korolev, Russia).

Results and discussion

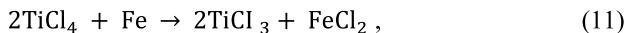
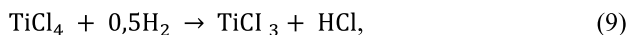
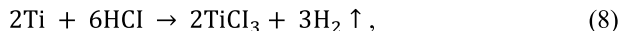
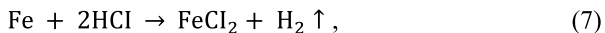
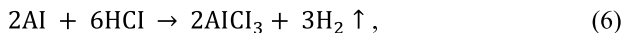
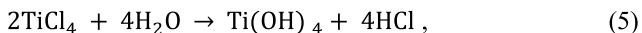
Table 1 depicts the chief parameters of the process of electrochemical synthesis of titanium trichloride using various reducing agents.

Table 1.

Parameters of electrochemical synthesis of titanium trichloride

Process parameters	Current density, A / dm ²								
	Al (AD-31)			Fe (St 3)			Ti (BT-0-1)		
Process time before the decomposition starts, in min	70	20	20	40	30	20	30	30	10
pH	3.0	2.0	2.4	2.5	2.7	2.6	2.05	1.96	2.0
T _{max} (°C)	44.3	63.0	58.3	30.1	42.6	50.1	43.0	41.5	34.2
m(Me) in solution (g)	0.66	0.37	0.47	2.26	2.43	2.08	0.64	0.65	0.68

When an electric current is passed through an aqueous solution of titanium tetrachloride, two processes may occur simultaneously, leading to the formation of titanium trichloride: hydrolytic (reactions 5–9) and redox (reactions 10–12).



Preparation of a polymerization catalyst (Ziegler-Natt reagent) and a precursor for the synthesis of nanodispersed titanium dioxide particles for the production of dye-sensitized solar cells. Considering the known data on the composition of the Ziegler-Natt reagent, one should conduct the process using aluminum electrodes. The diagram (Fig. 1) shows the data on the calculated yield of titanium trichloride (obtained based on the consumption of the aluminum electrode) and the actual yield of titanium trichloride based on the result analysis.

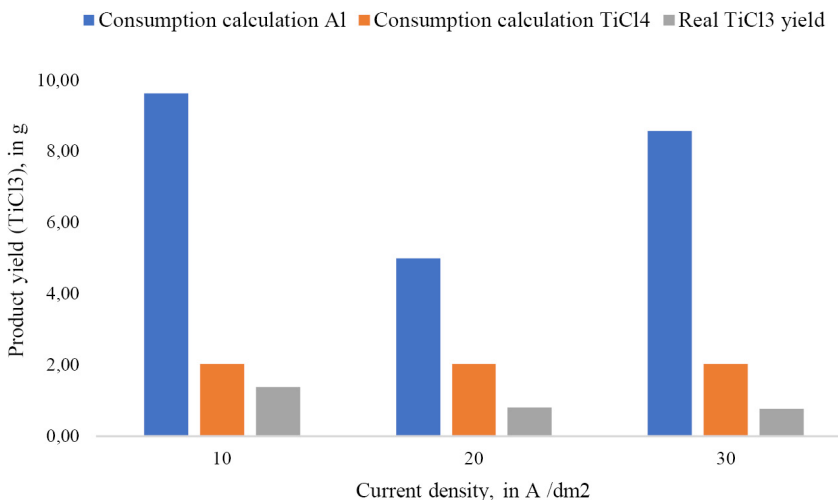
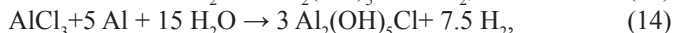
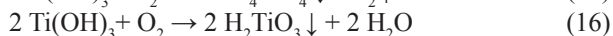
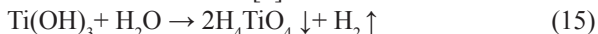


Fig. 1. The calculated and practical yield of titanium trichloride (Al electrode)

In Fig. 1 data, one can observe that the yield of titanium trichloride calculated from the mass defect of the aluminum electrode significantly exceeds its actual content and the maximum possible amount calculated from the decrease in the content of titanium tetrachloride, which may indicate the formation of aluminum oxychlorides (reactions 13–14).



One should note that the yield of titanium trichloride decreases with increasing the current strength, which is most likely due to the catalytic effect of temperature on the course of reactions 14–15 [3].



The yield of titanium trichloride ranges from 65 % to 35 % for 10 A/dm² and 30 A/dm², respectively. The resulting solutions can theoretically be used as a primary catalyst component of a Ziegler-Natta catalyst. Aluminum oxychloride, which is part of the solutions, will act as a co-catalyst for polymerization and titanium (III) chloride [3; 7]. The resulting solutions can also be used as a precursor in the production of coatings (nano dispersed titanium dioxide particles) for dye-sensitized solar cells. However, their preliminary partial purification from aluminum compounds may be required.

Preparation of a complex coagulant-reducing agent. The primary goal of this part of the research [4] is to evaluate the possibility of using solutions containing titanium trichloride and obtained by electrochemical dissolution of iron as a reagent for the purification of chromium-containing waters of electroplating production. Similar to the experiments with aluminum, the theoretical and experimental yields of titanium trichloride are compared. The obtained results are shown in the diagram (Fig. 2).

One should note the high reactivity of iron at all current densities, leading to a relatively higher yield of products than the previous experiment. The increased yield of titanium trichloride is also due to the lower process temperature and synthesis time (Table 1). The yield of titanium trichloride is 76%–66 % for 10 A/dm² and 30 A/dm², respectively.

The resulting solution contains iron (II) compounds, which together with titanium (III) chloride will act as a complex coagulant-reducing agent. The chromium (III) compounds formed during the reduction process are precipitated at pH 8.5 in the form of poorly soluble hydroxides. The synergistic effect of the combined use of iron and titanium compounds in wastewater treatment processes from chromium (VI) compounds is depicted in the diagram in Fig. 3.

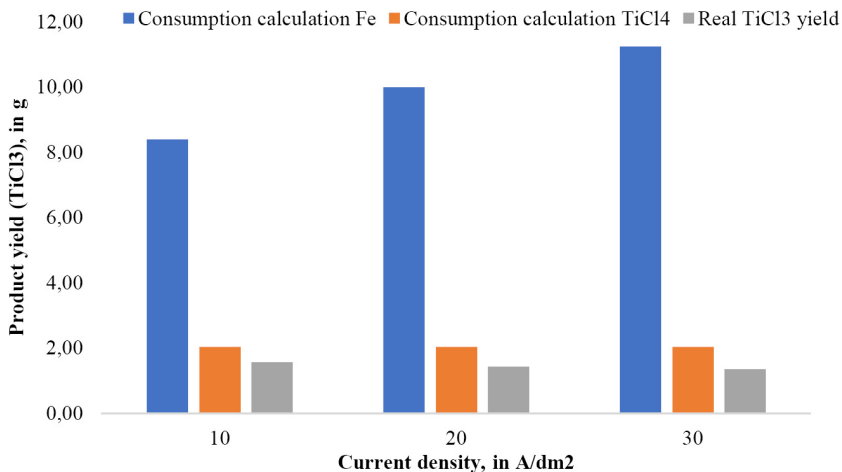


Fig. 2. Estimated and practical yields of titanium trichloride (Fe electrode.)

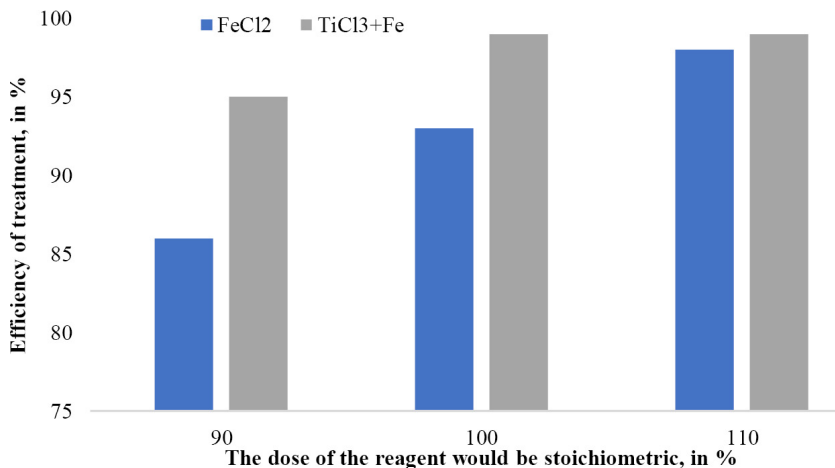


Fig. 3. The efficiency of wastewater treatment from chromium (VI) ions

Based on the data presented in Fig. 3, one can conclude that solutions containing both titanium (III) and iron (II) chlorides are highly promising in wastewater treatment processes from chromium (VI) compounds. The filtration rate of the coagulation sludge (when using a Fe/Ti solution) is on average 1.5–2.0 times higher than with traditional reagents based on iron (II) chloride. The sed-

iment volume is minimal, and the sediment is easily filtered. Improved efficiency and increased speed of separation of coagulation slurries will significantly reduce the size of the treatment equipment and increase the economic feasibility of using the obtained solutions in the processes of wastewater treatment of electroplating production.

High-frequency titanium trichloride production. The primary goal of the experiment is to obtain high-purity solutions of titanium trichloride. Unfortunately, the previously obtained samples of titanium trichloride cannot be used in analytical chemistry, radioelectronic or optical fields due to the insufficient purity of the resulting reagent. To solve this issue, one should assess the possibility of conducting the electrochemical synthesis of titanium (III) chloride using titanium electrodes (Fig. 4).

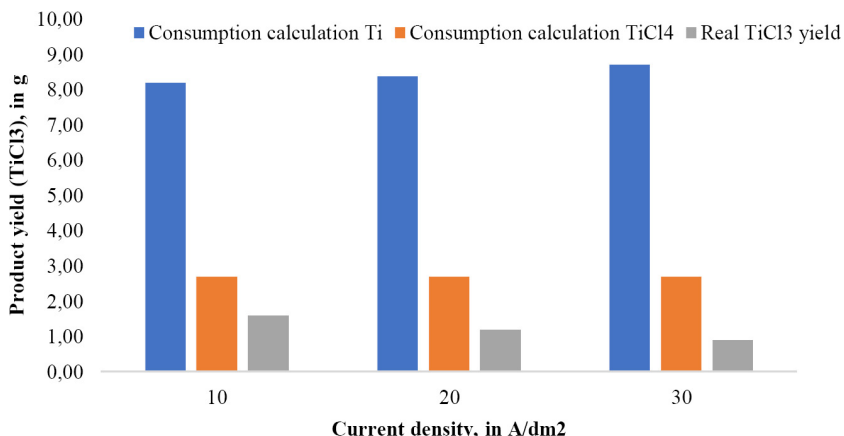


Fig. 4. Assessed and practical yield of titanium trichloride (Ti electrode)

One can observe from the data in Table 1 and Fig. 4 that the amount of dissolved titanium is practically independent of the current density, while the process conditions (pH and temperature) remain unchanged. The obtained values are associated with the anodic passivation of titanium; as a result, the metal surface moves into an inactive state. The yield of titanium trichloride is 59%–33% for the 10 A/dm² and 30 A/dm², respectively.

Despite the passivation of the electrode, due to the absence of foreign impurities in the solution, the resulting titanium trichloride is suitable for analytical purposes, as well as a starting reagent for the production of high-frequency titanium dioxide nanoparticles (for example, for the production DSSC).

Conclusion

Based on the results obtained in the paper, one can conclude that for the production of titanium trichloride – a catalyst for the synthesis of linear unbranched polymers of ethylene hydrocarbons – as well as for the organic synthesis and production of solar cells, it is preferable to use metallic aluminum as a reducing electrode. In contrast to the thermal method of preparation, this variant is characterized by a low heating temperature of the reaction medium, which increases the yield of the target product and its stability.

To obtain a reagent for wastewater treatment, one can use iron electrodes as a reducing agent. The high reactivity of Fe makes it possible to obtain a good yield of the target Fe-Ti component, and the low price of iron electrodes will further reduce the cost of a complex coagulant based on titanium trichloride. To further reduce the reagent cost, one should implement substandard solutions of titanium tetrachloride contaminated with silicon tetrachloride.

For the production of high-purity titanium trichloride, electrochemical reduction technology using titanium metal will be preferred. The synthesis product will be significantly lower in terms of the cost of titanium trichloride obtained by classical methods by simplifying the production scheme and reducing energy costs.

The undoubted advantage of the proposed technology for the production of titanium trichloride is the simplicity of the hardware design and environmental and industrial safety. Therefore, the technology of electrochemical reduction of an aqueous solution of titanium tetrachloride can become an excellent alternative to existing technologies, and depending on the chosen reductant, and it can meet the needs of titanium (III) chloride in various industries.

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