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Hydrofluoride method of complex processing of titanium-containing raw materials

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ABSTRACT

The paper briefly describes the hydrofluoride method of complex processing of titanium-containing raw materials, which was developed at the Institute of Chemistry of the Far Eastern Branch of the Russian Academy of Sciences, to produce titanium dioxide and iron (III) oxide.

1. Introduction

It is known that 90-95% of titanium raw materials in the world are annually used to produce pigmentary titanium dioxide. Pigments based on titanium dioxide of various grades are used in the manufacture of paints, paper, plastics, ceramics and other materials (Fig. 1). The demand for pigmented titanium dioxide depends on the ever-increasing volumes of housing construction, making cars, ocean vessels, aircrafts and other products that require persistent, durable coatings. The main consumers of titanium dioxide are China, India, USA, Japan, Germany [1]. Another significant area of application of titanium raw materials is the production of titanium sponge, an intermediate product for the production of metallic titanium and its alloys.

According to USGS, in 2013 the world's capacity for the production of pigmentary TiO_2 was about 6.6 million tons/year, of which 71% were in China, USA, Germany, UK and Japan. According to Ceresana company, it is forecast that by 2019 the capacity for the production of titanium dioxide will reach 7.5 million tons/year [4].

Currently, the production of titanium dioxide is carried out by two main methods - sulfuric acid (sulfate) and chloride, being approximately equal globally. Until the first half of the last century, the production of titanium dioxide was mainly based on the decomposition of titanium-containing concentrates by sulfuric acid (the method was developed in Russia in 1908-1918). Then, since the 1950s, the method of chlorination of titanium raw materials in pigmentary production, developed by an American company DuPont, has been successfully applied and implemented in many countries of the world.

Many papers describe in detail the technologies for the production of titanium dioxide, the requirements for the quality of the initial titanium-containing raw materials, the methods for utilization of industrial waste, the technological production schemes, the consumption rates of raw materials and reagents, and the prospects for improving production, both in sulfuric and chloride methods. The advantages and disadvantages of the two ways of producing pigmentary titanium dioxide can be analyzed on the basis of the data presented in Refs. [5-8]. According to many researchers, both sulfuric and chlorine methods for the production of pigmentary titanium dioxide are rather complex, since a large number of technological processes are involved in production, but the main disadvantage of these technologies is their environmental burden in the area where the pigment is produced.

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The development and introduction of alternative technologies for the production of pigmentary grade titanium dioxide from titanium-containing raw materials is still topical and timely.

One of the promising developments in this direction is research on the development of the physicochemical basis of fluoride technology. The first works on this topic date back to the early 1930s [9, 10].

2. Achieved results

To date, the information available in the scientific literature on the fluoride methods of processing titanium-containing raw materials makes it possible to single out two main directions. The first direction, based on the ability of fluoride compounds of titanium to sublimate under heating in vacuum or in gas media (free of water vapor), includes the steps of fluorination of titanium raw materials, separation of the main components of titanium and iron, followed by pyrohydrolysis of the iron-containing residue at a temperature of 300-600°C, obtaining iron oxide, pyrohydrolysis of the obtained titanium salts at temperatures up to 900°C. The second direction, which includes the fluoridation stages of the raw materials to produce fluorocomplexes of titanium and iron and the separation of the latter, is based on their different solubility in aqueous solutions followed by pyrohydrolysis of separately fluorine complexes of iron at temperatures up to 600°C and titanium fluorocomplexes at temperatures up to 900°C [11- 13].

The second, hydrofluoride method developed at the Institute of Chemistry of the Far Eastern Branch of the Russian Academy of Sciences can be easily adapted to any kind of titanium-containing raw materials, including radioactive minerals such as monazite, and allows obtaining with certain purity both titanium dioxide and iron oxides, concentrates of unreacted minerals, while the opening reagent (fluoride/ammonium hydrofluoride) is returned to the process cycle.

In the developed hydrofluoride method, the principal block diagram of which is shown in Fig. 2 [14], the process of fluorination of the raw materials occurs at sufficiently low temperatures (not higher than 140°C) and, depending on the composition of the raw materials, it makes it possible to control the temperature and the time of fluorination, which makes it possible to isolate in some subsequent stages some refractory minerals [15-21].

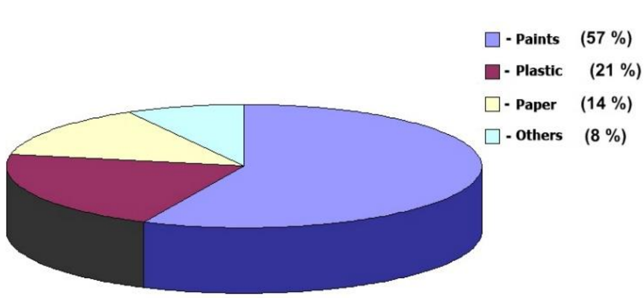

Fig. 1 - Structure of global titanium dioxide consumption [2, 3].

The maximum separation of fluorine-ammonium salts of titanium and iron occurs in solution due to the different solubility of complex salts in the aqueous solution against a background of a certain concentration of ammonium fluoride. The data on purification of fluorine-ammonium salts of titanium from chromophore trace impurities, primarily iron, are presented in Refs. [21, 22], namely by introducing into the solution hydrogen peroxide or by partial hydrolysis of a fluorine-ammonium solution at pH 7. The purified solution of the titanium salt is hydrolyzed, followed by stepwise pyrohydrolysis of the obtained hydrolysis product at a temperature of up to 850-900°C. The fluorine-ammonium salts of iron, if necessary, can be further purified from magnesium and calcium fluorides. Purification of fluorine-ammonium iron salts is carried out by dissolving them in a 20% solution of hydrofluoric acid, followed by separation of the residual fluorides of magnesium and calcium. A purified ammonium hexafluoroferrate salt is obtained from the fluoride solution by salting out the ammonia solution, which undergoes pyrohydrolysis to a temperature of 600°C. The resulting ammonia, water and hydrogen fluoride are utilized in scrubbers and subsequently, after evaporation, the resulting fluorine-ammonium salt is returned to the decomposition stage of the primary materials. It should also be noted that the use of fluorine-ammonium salts significantly reduces the hazard of work. The resulting oxides, especially titanium dioxide, depending on their purpose, can be surface treated with inorganic and organic compounds according to known technological schemes by various chemical compounds [6], or new compositions for the production of pigments with desired properties can be proposed. Advantages of the hydrofluoride method of processing titanium-containing raw materials seem to be undeniable, but it is necessary to create the appropriate process equipment and to ensure environmental safety of the entire technological cycle.

The hydrofluoride method [14-19, 23] was tested in laboratory conditions on many samples of ilmenite concentrates from various deposits in the Russian Federation, Ukraine, New Zealand, China, as well as perovskite concentrate [24]. It has been established that samples of ilmenite concentrates from various deposits having different elemental composition along impurity elements can be efficiently processed by the hydrofluoride method to produce pigments. It was shown in Refs. [25-28] that titanium dioxide obtained by hydrofluoride technology is superior to the known analogues of titanium dioxide obtained by other methods in its resistance to the action of ultraviolet radiation. But there are still many unresolved issues related to the behavior of the fluoride salts of the chemical elements present in the ilmenite concentrate in the form of microimpurities that pass into the solution together with titanium compounds. The study of such systems provides for obtaining data on the mutual influence of salt concentration, temperature, pressure, and other external factors on their solubility. The isolation of the necessary purity of a given salt from aqueous multicomponent salt solutions is of scientific and practical interest, and studies in this direction are topical.

The economic efficiency of the developed hydrofluoride method for the production of titanium dioxide is expedient to compare with the cost of producing 1000 tons of TiO_2 by the chlorine and fluoride methods, but unfortunately there are no approved technological equipment, experimental production data for the hydrofluoride technology, therefore, it is possible to compare only the above main technological operations, and they are all in favor of the fluoride method. In the fluoride method, there is one high-temperature operation pyrohydrolysis of salts or hydrated products; in the chlorine method, there are three. In addition, the process of grinding the final product obtained by the chlorine method is very laborious.

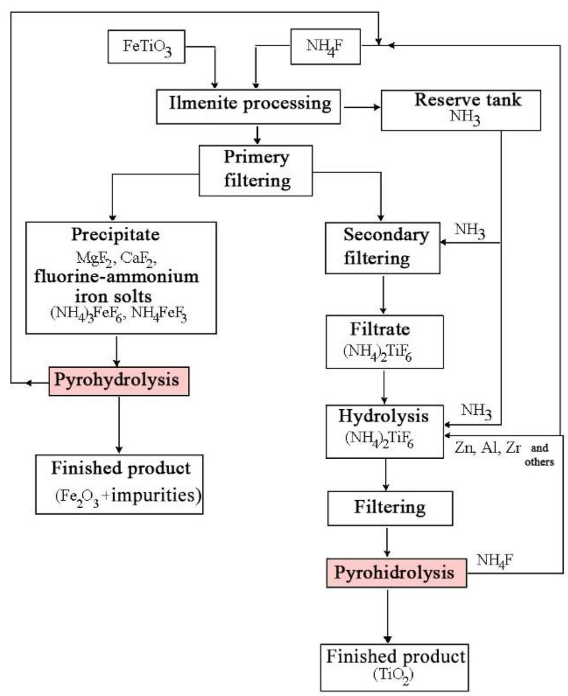

Fig. 2 - Scheme of technological operations in the hydrofluoride process for the production of titanium dioxide and iron oxides.

To obtain 1,000 kg of TiO_2 for all analyzed technological schemes, approximately 2,000 kg of ilmenite is needed. The costs of additional materials and energy costs for the sulfuric acid method are presented in the literature in detail. The energy costs for chlorine production depend on the stage from which they are formed: from the processing of ilmenite or from the processing of $TiCl_4$. If a slag highly enriched in TiO_2 (at least 80%) from is prepared ilmenite for subsequent chlorination, this operation alone will require up to 3,000-5,000 kW/h for processing one ton of the primary materials.

The energy costs for the main operations for the proposed hydrofluoride processing scheme are approximately 5,000 kW/h, and at the same time, ~ 500 kg TiO_2 and ~ 500 kg Fe_2O_3 are obtained.

3. Conclusion

The Institute of Chemistry of the Far East Branch of the Russian Academy of Sciences developed the physicochemical basis and the technological scheme for an ecologically acceptable, non-waste hydrofluoride method for processing ilmenite concentrates to produce pigments based on titanium dioxide and iron oxides, and return of opening reagents (fluorine-ammonium salts) in the technological cycle; all at minimal water consumption. An approximate calculation of the cost of one ton of pigmentary TiO_2, obtained by the proposed technology, is no more than half of its world average. The establishment of pigment production on the basis of hydrofluoride technology enables to cover not only Russia's domestic needs, but also to offer pigment for export, since by its parameters, first of all, by its resistance to ultraviolet radiation, it will surpass the best world analogs. To carry out chemical and technological research and develop a feasibility study of industrial technology for the hydrofluoride process of a complex non-waste technology for the production of pigments from titanium-containing raw materials, in the stead of existing ones, it is necessary to create a pilot technological line with non-standard equipment. Materials for their manufacturing have been selected, and their behavior in fluoride media has been studied.

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