TITANIUM-CONTAINING FILLERS. PRODUCTION AND PROPERTIES

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Abstract

Physico-chemical processes and properties of titanium-containing oxide composites (titanosilicate), obtained by joint precipitation or ultrafine grinding of the components, have been explored. Conditions of direct synthesis of the composites of predetermined composition, structure and grain size, providing good operational features for the fillers, have been determined. The resulting nano-size composite powders either consist of titanium(IV) dioxide of the rutile ore anatase modifications, incorporated into an X-ray amorphous silica matrix, or of particles with a titanium(IV) dioxide nucleus inside a silica shell. The composites are characterized by a narrow size distribution and properties that make them attractive components for various functional materials. Using in synthesis of mostly technical materials, rather than pure, reagents reduces the fillers cost and extends the area of their application.

Key words: *grinding, mechanical activation, thermolysis, composite, titanium dioxide, silica, homogeneous composition, grain size, morphological properties.*

1. INTRODUCTION

Inorganic fillers are widely used in manufacture of lacquer-and-paint and building materials, paper, plastic, insulating and protecting materials, etc. [Chuppina & Zhabrev 2009; Gerasimova & Skorokhodova 2011; Gerasimova et al. 2014; Mudrov, Savchenko & Shitov 1981]. The materials' performance largely relies on the composition and physical-technical properties of the fillers, which are, in one way or another, affected by synthesis methods. Thus, diminishing of the particle sizes increases the homogeneity of the initial composition, which leads to lower power consumption in manufacture of the filler-based materials. Each filler is individual in its properties, which improves the quality of target products. Sometimes the initial composition contains not one but several synthetic fillers. The composition of the aforementioned materials is admixed with titanium dioxide of the rutile modification and silicon dioxide. Since the technology of these products incorporates complicated process stages [Belenky & Riskin 1974; Mayorov 2001], their cost is fairly high. Viewed in this way, the composite fillers have several advantages. Firstly, they can be obtained from mineral and chemical by-products, that is, at lower material expenditures. Secondly, such composites not only retain the properties of their component parts, but acquire some new properties that often improve their performance. Admixing of the fillers to the other formulation components during dispersing diminishes both the process time and power consumption.

In this work we have investigated the process conditions of composite titanium and silicon oxide based-fillers, the morphological properties of the particle surfaces, their composition and properties.

2. EXPERIMENTAL

The materials used in this study were the sphene concentrate (calcium titanium silicate - CaSiTiO5), the titanium salt (titanium(IV) ammonium sulphate – $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ – (TAS)), the hydrated titanium silicate precipitate (TSP), titanium dioxide (anatase), silicon dioxide, and chemically pure zinc oxide. Some of the components' characteristics are presented in Table 1.

Table 1. Characteristics of the objects of research

Materials	Characteristics
Sphene concentrate	Content of TiO_2 not less than 30%, particle size <40 μm
$(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ – (TAS)	Content of TiO_2 20,8%
TSP– titanium silicate precipitate	Content of volatile components, wt.% – 24.5, TiO_2-63.2, SiO_2-11.3 phases: rutile + anatase and x-ray amorphous silica
Titanium dioxide	Content of TiO_2 - 96%, S_A - 3.61m^2/g, anatase, particle size 2-50 μm
Silicon dioxide (silica)	Content of SiO_2 – 92.8% , S_A – 38.9 m^2/g, particle size 0.5-15 μm

The hydrated titanium silicate precipitate (TSP) was the product of sphene interaction with 30-32% hydrochloric acid in a boiling condition for 10 h by the reaction:

$CaTiSiO_5+2HCl= \downarrow TiO_2 \cdot SiO_2 \cdot nH_2O + CaCl_2$

These conditions promote the formation of a hydrated precipitate of a complex composition. Calcium remained in the hydrochloric acid phase due to its high solubility [Gerasimova, Maslova & Shchukina 2009]. The precipitate was thoroughly washed with water and thermally treated at 650-900°C to obtain a titanium silicate composite.

Another method to obtain the composite of interest incorporates ultrafine grinding of a mixture consisting of anatase and silica. Anatase was obtained by thermolysis of a titanium salt, TAS [Gerasimova et al. 2014] which was isolated by crystallizing from a titanium(IV) sulphate solution emerging as a result of sphene interaction with sulphuric acid [Lazareva et al. 2006; Maslova, Gerasimova & Morov 2002]. The desalinating agent was ammonium sulphate solid.

$CaTiSiO_5+H_2SO_4 = \downarrow CaSO_4 \cdot SiO_2 \cdot nH_2O + TiOSO_4$

$TiOSO_4 + (NH_4)_2SO_4 + nH_2O = \downarrow (NH_4)_2TiO(SO_4)_2 \cdot nH_2O$

The crystallization conditions are described in work [Motov & Godneva 2009]. The TAS thermolysis was conducted at 850°C.

The component mix was ground in a planetary mill of the Pulvirsette-7 type. The grinding containers (4) had the capacity of 50 ml; the titanium balls were 10 mm in diameter. Both the containers' walls and the balls were made from titanium. The rate of the container revolution was 5000 rev/min. The ratio of the balls and ground material was 10:1. The quantity of the ground material was 6 g per one container. The mechanical activation lasted for 1 h and then the homogenized mixture was subjected to thermolysis. This grinding method is adjustable with mechanical activation of solid materials and is therefore widely used in chemical technology [Avvakumov, Kalinkin & Kalinkina 2009; Gerasimova, Maslova & Shchukina 2010; Kalinkin 2007].

Samples of initial, intermediate and target products were analyzed using the chemical and physical-chemical methods. The phase composition was determined using the XRD and DTA analyses. The XRD patterns were recorded at a Shimadzu equipment at a rate of 0.02 deg/sec within the 2θ=6-180° range. The DTA/DSC data were collected using high-resolution thermogravimetric analyzer (Netzch STA 409 PC/PG) under argon atmosphere. The amount of weight loss and the heat flow were recorded in the range 25-1000oC with a Pt – PtRh thermocouple at a rate of 10oC/min with an Al_2O_3 reference electrode. The analyses also involved a scanning electronic microscope SEM LEO 420. The surface properties were determined by the BET method using a TriStar 3020 analyzer. The chemical composition, including the microimpurities, was determined using the X-ray fluorescent analysis at a MAKS-GV spectroscope.

3. RESULTS AND DISCUSSION

3.1. Production of a titanium silicate composite from TSP

The thermal treatment regime (thermolysis) was selected by calcining a TSP sample in a muffle furnace at 650, 750 and 900°C for 2.5 h. The calcined product was ground in a laboratory vibratory mill after which its phase composition and some of the properties were determined using the known methods (pH of aqueous extract, water-soluble compounds (WSC), organophilicity (OF), reducing power (R), water-retaining capacity (W)) [Livshits 1987].

As can be seen in Table 2, increasing of the TSP thermolysis temperature is accompanied by converting of anatase to the rutile phase with a stable crystalline structure. At temperatures higher than 750°C, anatase is not present in the solid phase composition.

Table. 2. Phase composition of precipitate

No	Thermal treatment regime	Phase composition
TSP init	Dried in air	Rutile + anatase, X-ray amorphous silica
1	TSP calcined at 650°C	Rutile + anatase, X-ray amorphous silica
2	TSP calcined at 750°C	Rutile, X-ray amorphous silica
3	TSP calcined at 900°C	Rutile, X-ray amorphous silica

Increasing of the temperature to 900oC results in compacting of the precipitate structure, which is evidenced by an abrupt reduction of the surface area value. The powder porosity diminishes about twofold, and the pore diameter increases (see Table 3). When calculating the particle sizes with account for their surface area, we used the formula $D=6/S_A.\cdot\rho$, where D is the particles diameter and ρ is the particles density. The particles diameter increases 1.5 with temperature increase.

Table 3. Surface properties and particle size of the samples

TSP treatment, T °C	S_A., m^2/g (BET)	Total pore volume, cm^3/g	Pore D, nm	Particle size, nm
650	19.98	0.066	9.41	102.3
750	20.84	0.070	11.85	112.8
900	7.28	0.036	21.63	154.1

Analysis of the TGA data presented in Figure 1 demonstrates that adsorption and crystallization water are removed at temperatures ranging from 69 to 345°C. Its total loss is 6.31%. Water is present in the TSP composition only as the little-hydrated components $MeO_2\cdot H_2O$, where Me is Si and Ti. The original structure of hydrated titanium dioxide is crystalline. It acquires its final form at temperatures a little exceeding 600°C at a mass loss of 2.31% (the exoeffect corresponding to the titanium oxochloride impurity is recorded at 547.1°C and that of anatase recrystallization to rutile – at 604.9°C). Presumably, the temperatures 650-750°C are sufficient for the formation of rutile structure of the titanium component.

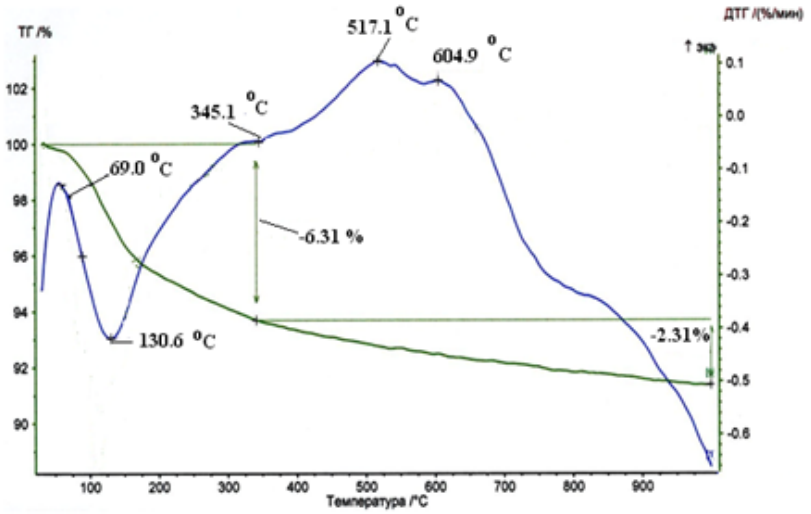


Figure 1. Thermogram of a TSP sample

Table 4 shows how the calcination regime of TSP affects the composite product properties.

Table 4. Properties of the composite

Calcining regime of TSP	WSC,%	pH	OF, g/100g of the product
650°C – 2h	2.05	5.60	27
650°C – 3.5h	0.89	6.51	25.4
750°C – 2h	0.45	6.88	28.6

It is evident from the values of WSC and pH aqueous extract that calcining of TSP at 650°C for 2 h is not sufficient to totally remove the acid anion (Cl^-) from the precipitate. The rate of chlorine removal can be increased by increasing the calcining time to 3.5h and temperature to 750°C, which accelerates the formation of rutile structure in titanium dioxide. The bulk density of the samples varies over a narrow range of 760 - 790 g/dm^3. This product can be used in manufacture of atmosphere-resistant silico-organic paint with enhanced thermo- and water-resistant properties [4].

3.2. Production of a titanium silicate composite from titanium and silicon oxides by ultrafine grinding

A weight of titanium dioxide obtained by TSP thermolysis was ground in a mechanical mill together with silica. The components mass ratio was TiO_2:SiO_2=1:0.1 and TiO_2:SiO_2=1:1. The prepared mixture was placed into a planetary mill for 1 h whereupon it was removed and its properties and composition were examined. XRD pattent has shown that the impact energy of grinding of a mix with an initial component ratio of TiO_2:SiO_2=1:0.1 causes deformation of the initial structure, while increasing of temperature at the impact point results in a 5-6% recrystallization of anatase to rutile (Fig.2a). This process is inhibited at higher silica contents in the mixture due to the fact that silica absorbs a part of the structure-transforming energy (Fig. 2b).

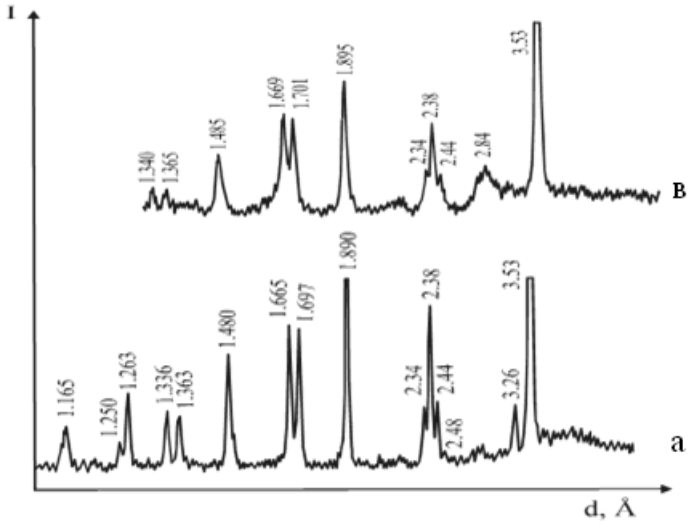


Figure 2. XRD patterns of the composites obtained from oxides with initial ratios of TiO_2:SiO_2: 1-1:1; 2 – 1:0.1.

The particle grain size of the ultra-ground oxides is nearly identical (Fig.3). The size of agglomerates made up of nano-sized crystallites varies over a narrow range and is characterized by the following values: 1.038-1.761 μm, 75% - 1.038-2.272 μm, with a maximum size not exceeding 10 μm.

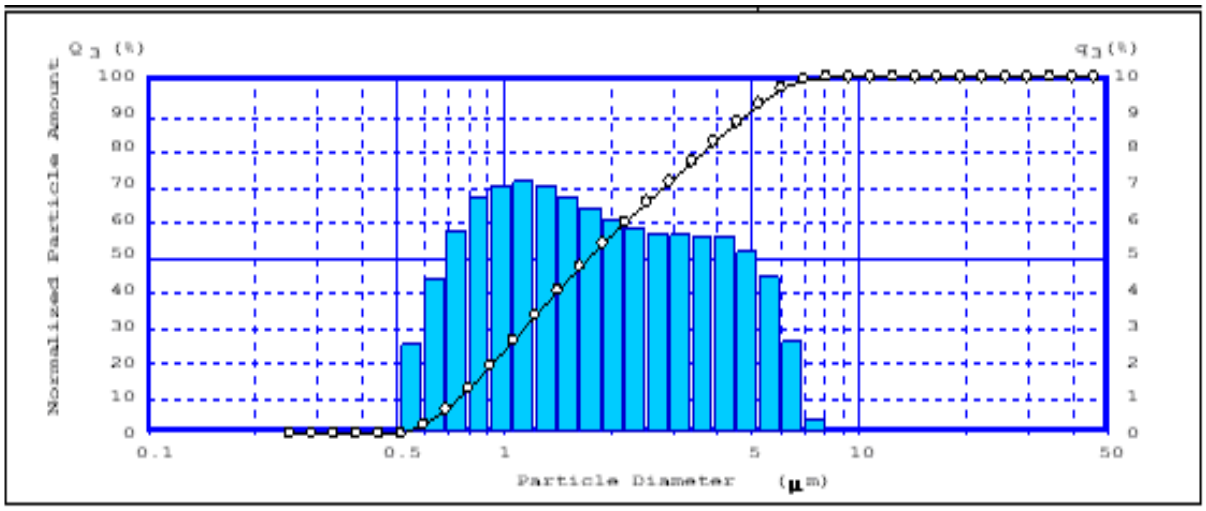
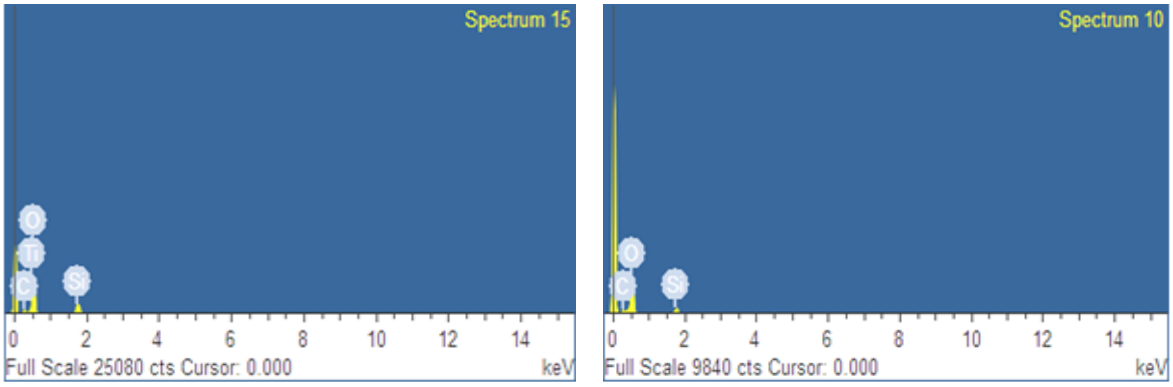


Figure 3. Particle size distribution in the powders after mechanical activation of a titanium dioxide and silica mixture.

The energy-dispersive analysis of a component mix (TiO_2:SiO_2= 1:1), performed prior to mechanical activation (Fig. 4-1) is indicative of a low activity of the surface layer, whereas its composition (Table 5) reflects the presence of titanium and silicon as oxides, at a small content of calcium carbonate on the surface. The particle size of the component mix varies between 5 to 50 μm (Fig. 5-1). The crystal sides are fairly well pronounced.



1 2

Figure 4. Energy-dispersive analysis of particles' surface: 1 - sample prior to mechanical activation, 2 – sample after mechanical activation

After the mechanical activation the energy activity of the surface increased considerably (Fig. 4-2) mainly due to amorthous silica. The presence of calcium carbonate, at a total absence of titanium (Table 5), suggests that the surface of the titanium particles is covered with a layer of amorphous silica (Fig. 5-2). The particle size in the sample with a shell-structure does not exceed 10 μm; the crystals face have smoothed.

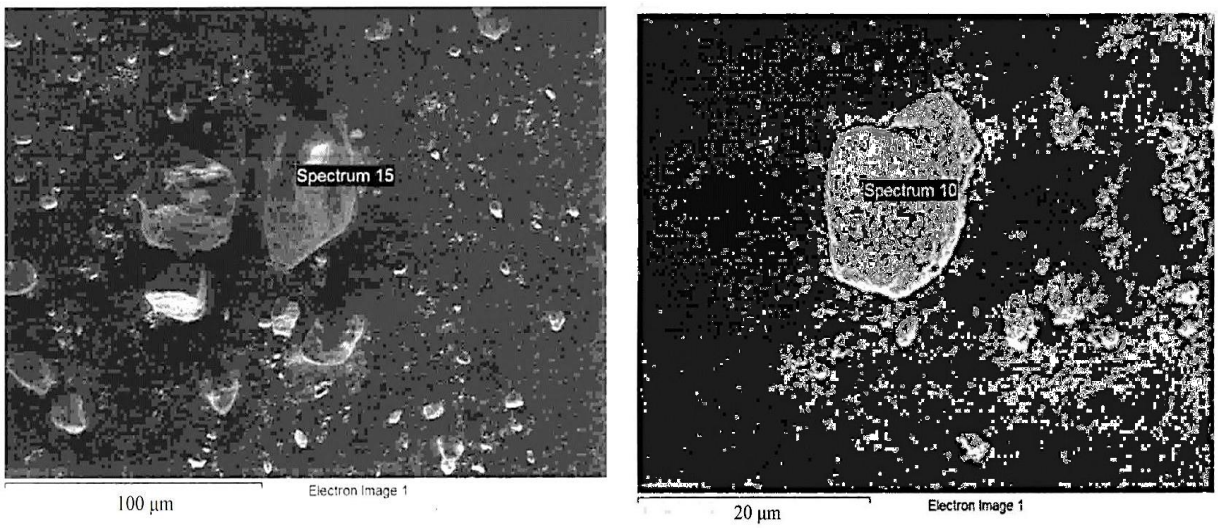


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Figure 5. SEM image of samples: 1 – particles prior to mechanical activation; 2 – particles after mechanical activation.

Table 5. Element composition of the particles surface

Element	Weight %	Atomic %	Weight %	Atomic %	Notes
	Prior to mechanical activation		After mechanical activation		
C	5.08	9.51	7.53	11.07	C $CaCO_3$
O	44.13	62.07	64.92	71.62	O SiO_2
Si	13.76	11.03	27.55	17.31	Si SiO_2
Ti	37.03	17.40	-	-	Ti Ti

As revealed by analysis of the morphological properties of the composites (Table 6), after mechanical activation the surface area increases by 30%, if the initial ratio is TiO_2:SiO_2=1:0.1, and decreases slightly if it is TiO_2:SiO_2=1:1 (compared to the initial mixture). The total pore volume is slightly higher in the composite containing more calcium. Judging by the pore sizes, the system is mesoporous.

Table 6. Surface properties of composites

TiO_2:SiO_2 in initial mixture	S_a, m^2/g (BET)	V_{pore}, cm^3/g	D_{av}, nm
1:0.1	10.80	0.080	20.61
1:1	25.75	0.103	16.93

The composition and properties of the composites obtained are shown in Table 7.

Table 7. Composition and properties of titanium silicate composites

TiO_2:SiO_2 in initial mixture	pH	WSC,%	OF, g/100g of the product	V, g/100g of the product	TiO_2,%	SiO_2,%	R
1:0.1	6.61	0,51	22,5	18,2	92.73	7.26	650
1:1	5.98	0,76	34,8	35,3	52.93	47.06	230

These composites can be used as components in the production of plastic, titanosilicate enamel, and building materials such as dry mix mortar, linoleum, etc.

4. CONCLUSION

By using available and low-cost precursors, we obtained the precursors for synthesis of composite pigment fillers of a titanium-silicate composition. Two pathways of synthesis have been investigated, one based on liquid-phase homogenizing (chemical reaction) and the other based on solid-phase homogenizing, i.e. mechanical activation. Conditions for direct synthesis of composites of a desired composition, structure and properties, ensuring high performance characteristics for the fillers, have been determined. The resulting nano-size composite powders consist of titanium(IV) dioxide of rutile or anatase modifications, incorporated into the silica X-ray amorphous matrix, or act as a carrier (nucleus) for a silica shell. The composites have a narrow grain size distribution and the properties allowing them to be used as components of various functional materials. Substituting of pure reagents for technical materials will diminish the fillers' cost and extend the area of their application.

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